Intermolecular Interactions between Medium-Sized Systems. Nonempirical and Empirical Calculations of Interaction Energies: Successes and Failures

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Received October 9, 1987 (Revised Manuscript Received February 5, 1988)

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I. Introduction

Four types of interactions are distinguished in physics: strong, electromagnetic, weak, and gravitational. Strong interactions between protons and neutrons result in the formation of atomic nuclei. Much weaker interactions between nuclei and electrons (called electromagnetic) lead to formation of atoms.

Weak interactions have been traditionally associated with subatomic phenomena but they act also between protons, neutrons, and electrons, i.e., between building units of atoms and molecules. In contrast to all other types of forces, weak forces distinguish between left- and right-handed systems. The gravitational interactions acting between all mass systems are well known. The ratio between the four types of forces are approximately equal to $1:10^{-3}:10^{-15}:10^{-40}$.

In chemistry, only electromagnetic forces are of fundamental importance. Roughly speaking they are manifested in the formation of covalent bonds between atoms (formation of molecules) and noncovalent bonds between molecules (formation of intermolecular associates). The former interactions are sometimes also termed strong and the latter are given a great variety of names, e.g., physical, weak, or van der Waals (vdW). However, using the terms strong and weak instead of covalent and noncovalent is misleading and leads to confusion in the nomenclature, which is already considerable in the field of vdW systems.

We would recommend the terms covalent and van der Waals interactions; the former are connected with the formation or decay of covalent bonds, the latter with the formation or decay of vdW bonds.

VdW interactions are much weaker than covalent interactions; the vdW bond is therefore graphically depicted by points (···) connecting the subsystems. There is a wide range of vdW molecules, from very strong, ionic vdW systems (e.g., $H_2O···Na^+$), with a stability approaching that of covalent molecules to very weak, "true" vdW molecules (e.g., He···He), with a potential energy curve depth about the same as the zero-point vibrational energy.

VdW systems can be formed from practically any type of system (molecules, ions, radicals) and are called vdW molecules, vdW ions, and vdW radicals. The number of vdW molecules is therefore practically unlimited. VdW systems that are very unusual from the viewpoint of classical structural concepts are sometimes formed; e.g., the pyridine···He complex has been detected in the gas phase. Let us add, however, that most of them are very short-lived at laboratory temperature. The energy of thermal motion of molecules at 300 K is about 2.5 kJ/mol; only stronger complexes have any chance of surviving.

The classification of vdW molecules should be briefly mentioned. They are most frequently distinguished on the basis of the leading stabilization energy term and can be divided into ionic complexes ($Li^+···HF$, ionic interaction), electrostatic complexes (LiF···LiF, electrostatic interaction), hydrogen-bonded (H-bonded)

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complexes ($H_2O\cdots HOH$, formation of H-bond), charge-transfer complexes (tetracyanoethylene··· benzene, charge-transfer interaction), and "true" vdW molecules (Ar···Ar, dispersion interaction). Sometimes the shape of complexes forms a basis for classification: stacking complexes possess subsystems in parallel planes.

The stabilization accompanying the formation of a covalent bond comes from the overlap either between partially occupied orbitals or between the HOMO of an electron donor and the LUMO of an electron acceptor. When a vdW bond is formed, the bonding orbitals of the interacting subsystems are completely occupied by electrons and all the antibonding orbitals are unoccupied. (Moreover, the gap between the occupied and unoccupied orbitals is large and the overlap between them is not significant.) Interaction between completely occupied orbitals leads to destabilization (repulsion). Where does the stabilization of vdW molecules come from? It originates from the interaction between permanent multipoles, between a permanent multipole, and an induced multipole or finally, between an instantaneous (time variable) multipole and an induced multipole; the respective energy terms are called Coulombic, induction, and dispersion. The second and third terms are attractive, and the Coulombic term is either attractive or repulsive, depending on the mutual orientation of the multipoles. The repulsion connected with the above-mentioned overlap of occupied orbitals is called exchange-repulsion. What is the relative importance of the individual terms? First, it depends on the distance between the components (subsystems) of the vdW system under study. Second, in the region of equilibrium distances, there are, e.g., numerous vdW molecules in which the Coulombic energy is dominant. In another important class of vdW molecules the dispersion energy dominates. Another major group of vdW systems are those containing a hydrogen bond. These complexes play a crucial role in chemistry and biology. It has been believed that the Coulombic energy is dominant in these complexes, while the induction and dispersion terms are less important. This concept is to some extend valid for small H-bonded complexes (e.g., $H_2O\cdots HOH$, HF···HF). It has been found, however, that the dispersion energy becomes more important for larger vdW molecules (e.g., the guanine dimer) and is sometimes even comparable to the Coulombic energy. In some very large complexes, the dispersion energy represents the dominant energy contribution.

II. Calculation of the Interaction Energy

The products of vdW and covalent interactions (vdW molecules and classical molecules) differ significantly. Here a question can be posed: Can quantum chemistry describe vdW interactions as successfully as covalent interactions? The answer is unambiguously "Yes". However, calculations in this field, as will be seen later, represent a very difficult task for quantum chemistry, simply because the energy changes accompanying formation of vdW systems are very small.

A. Variation and Perturbation Methods

As in other regions of quantum mechanics and in quantum chemistry as a whole, both the methods for the approximate solution of the Schrödinger equation—the variation and perturbation methods—are crucial to the study of vdW interactions.

In the variation method, the interaction energy, ΔE, accompanying the formation of a supersystem by association of the subsystems, is given as the difference between the energies of the supersystem (E^T) and of the subsystems (the energy of the ith subsystem is E_i):

$$\Delta E = E^{T} - \sum_i E_i \quad (1)$$

Unfortunately the values of E^T and $\sum_i E_i$ differ only by tenths to thousandths of J/mol and the value of E^T for small and medium complexes amounts to 10^6–10^{10} J/mol. The energies of the subsystems and of the supersystem must be calculated to at least seven to eight significant figures, so that the calculation is rather complex. Another problem of the variational method originates from the fact that only energies E^T and E_i (eq 1) are bounded variationally; their difference, ΔE, is, however, not bounded variationally. Interaction energy is constructed as the sum of the Hartree–Fock (HF) interaction energy (ΔE^{HF}) and the correlation interaction energy (ΔE^{COR}). Although the correlation energy constitutes only a small portion (a few percent) of the total energy of the subsystems and of the supersystem, the role of the correlation contribution to the interaction energy is very important. There are no types of vdW molecules for which the correlation contribution could be neglected. At first glance, the perturbation method appears far more suitable for describing vdW interactions. The interaction energy is calculated directly, rather than as a difference between two large, almost identical numbers. ΔE is expressed as a sum of the contributions from at least the first- and second-order perturbation calculations: Coulombic (E^C), exchange-repulsion (E^{ER}) (first order), induction (E^I), dispersion (E^D), exchange-induction (E^{EI}), and exchange-dispersion (E^{ED}) (second order).

Despite of the problem inherent in the variation evaluation of the interaction energy, the vast majority of the calculations of the interaction energies of various types of vdW molecules are carried out by using this method. This is because the variation calculation is formally simple and straightforward and because standard quantum chemical computer programs can be employed. An important advantage of the variation approach (also called supermolecular) is the fact that it is valid for any distance between the subsystems and, further, that higher order terms with respect to the interaction potential are naturally implicitly taken into account. On the other hand, the perturbation approach is advantageous in that the individual contributions to the interaction energy have a clear physical meaning. The perturbation calculation (tedious even for very small vdW molecules) is therefore used for those vdW molecules, where a deeper insight into the nature of the vdW interaction is necessary.

What is the relationships between the interaction energies evaluated by using the variation (supermolecular) and perturbation methods? Let us assume that the perturbation calculation was performed through the higher orders. The supermolecular ΔE^{HF} value will be practically identical[1] with the sum of the perturbation terms E^C, E^{ER}, E^I, and E^{EI}. In order to understand the relationship between ΔE^{COR} and its perturbation analogue, it is necessary to analyze the origin of ΔE^{COR}. With respect to the electron excitation type within the supersystem, we can distinguish the intersystem and intrasystem contributions to the interaction correlation energy. The former term originates from double excitations within the supersystem, i.e., excitation of a single electron from each subsystem; either of the virtual space then contains an electron. The latter term, the change in the intrasystem correlation energy (i.e., the change due to the varying distance between the subsystems), results from double excitations; both electrons pass together into the virtual space of either subsystem. The intersystem contribution is always attractive and corresponds to the sum of the dispersion and exchange-dispersion energies. The intrasystem term may be attractive or repulsive and corresponds to the correlation corrections to the Coulombic and exchange-repulsion energies. This term can be important for some vdW molecules and must not be neglected in accurate calculations.

B. Comparison between the Calculated and Observed Interaction Energies

The agreement between the calculated and experimental stabilization energies is a good measure of the success of the theoretical approach used. A difficulty, however, lies in the fact that the experimental determination of the stabilization energy is not unambiguous. Let us demonstrate this situation on what is probably the most frequently studied vdW molecule, the water dimer. The stabilization energies, determined by different experimental techniques, lie in a rather broad interval from −12.13 kJ/mol[2] to −28.03 kJ/mol.[3] Two recent values are rather similar, −22.30 ± 2.09 kJ/mol[4] and −23.01 kJ/mol[5] (the measurement of the thermal conductivity of water vapor yielded an interaction enthalpy at 373 K of −15.02 ± 2.09 kJ/mol; interaction energy given above were deduced from the zero-point and thermal energies presented in ref 6). The range of experimental values is so broad that almost all theoretical values fit into the interval. It seems that the most reliable is the value found from thermal conductivity measurements;[4] however, the experimental error is rather large and prevents reliable selection among the theoretical procedures (see, e.g., the conclusion on $(H_2O)_2$ in ref 6 and the discussion in ref 7). Finally, great care must be taken that comparison with experimental values includes a careful analysis of all the possible sources or errors in the theoretical calculation (special attention should be paid to the far-reaching compensation of errors) and thorough evaluation of the experimental data. This is a significant point in the whole field of theoretical chemistry and plays an extremely important role in the evaluation of interaction energies (see, e.g., the discussion on $(He)_2$ in ref 8).

C. Classification of vdW Systems

The size of vdW systems currently being studied range from two helium atoms to oligomers of proteins and nucleic acids. With reference to contemporary computational facilities, it is expedient to distinguish between small (up to four atoms, up to 10 electrons), medium (dozens atoms, hundreds electrons), and large (10^3 atoms, 10^4 electrons) systems, polymers including colloids (atomic structure is neglected), and supramolecular structures. For each group of vdW molecules, it is necessary to work at a different level of sophistication, leading, of course, to results of varying quality. The first group of vdW molecules can be studied by employing the most accurate nonempirical methods of quantum chemistry in connection with an extended basis set. For these systems we expect to obtain accurate values of the stabilization energies and other characteristics of vdW molecules, closely related to the experimental values. If the experimental values are lacking, it is possible to safely use theoretical, i.e., quantum chemical, values. The vdW molecules in the second group are relatively large, preventing the use of methods and basis sets in the previous group. Let us stress that combination of sophisticated theoretical procedures with small (poor) basis sets leads to meaningless results. If a consistent method and basis set are used, we can obtain reliable relative values of the interaction energies and other characteristics. The theoretical procedures used in the remaining groups are mostly of a semiempirical or empirical character, and hence care must be taken when considering the calculated characteristics.

III. Small Systems

Small vdW systems were discussed in detail by Chałasinski and Gutowski in the preceding review.[9] The authors[9] have pointed out the very serious problems connected with accurate evaluation of the stabilization energy for small vdW systems. Extrapolating these problems to larger vdW systems creates a feeling of hopeless. There is, however, valid reason for being optimistic in the calculation of the stabilization energy. Almost all the vdW systems discussed in the above review[9] were "true" vdW molecules, i.e., complexes where the dominant stabilization comes from the beyond Hartree–Fock energy. As will be seen in the next chapter, accurate calculations of this part of the interaction energy are very tedious, because of difficulties connected with the choice of both the theoretical procedure and the AO basis set. In some instances is the HF interaction energy dominant. This is true for medium-sized H-bonded complexes. To calculate the ΔE^{HF} accurately is a much easier task: the choice of the theoretical procedure (Hartree–Fock method) and of the basis set (DZ+P is usually sufficient) is straightforward.

IV. Medium-Sized Systems: Comments on and Criticism of Currently Used Computational Procedures

A. Nonempirical Methods

The interaction energy (eq 1) is determined as the difference between the energy of the vdW molecule and the sum of the energies of the subsystems. In addition to the problem of high accuracy (see above), the determination of the interaction energy in this way involves one very important requirement, which, at first glance, seems to be trivial. The energies of the supersystem and subsystems should be evaluated in a consistent way because only then does their difference (i.e., the interaction energy) include terms reflecting physical effects. Two examples of potential inconsistency will be discussed in detail: basis set inconsistency, which is connected with a very important basis set superposition error, and size inconsistency, which corresponds to an incorrect dependence of the theoretical method on the number of particles.

1. Basis Set Superposition Error

To understand the mere fact of basis set inconsistency is not easy. Let us suppose that a supersystem and subsystems are described by the same basis set, as in standard evaluations of the interaction energy. It would appear that there is no basis set inconsistency. This is not true, because the supersystem is described by a larger basis set, by a set which is formed by superposition of the basis sets of the two subsystems (cf. Figure 1). Larger basis set of the supersystem inevitably yields a larger total energy and, consequently, larger interaction energy. The increase in the total energy of the supersystem as a result of the unequal basis sets of the supersystem and the subsystem is called the basis set superposition error (BSSE). This error has nothing in common with the physical effects of interaction but is an artificial mathematical effect. Immediately, the question arises of what a consistent basis set would be. The subsystems should be described by the basis set of the supersystem. In this case there will be no superposition of basis sets for the supersystem, and consequently the BSSE will be equal to zero. Almost 20 years ago, Boys and Bernardi[10] introduced the "function counterpoise" method for eliminating the BSSE; the same basis set is used for the subsystem as for the supersystem. Clearly, the BSSE is geometry dependent; hence, it is necessary to evaluate it for each mutual distance and orientation of the subsystems. Furthermore, only size-consistent methods can be used for evaluation of the energies. The interaction energy, corrected for the BSSE (ΔE_C) follows from the following equation:

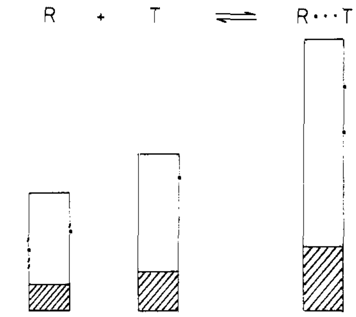


Figure 1. Superposition of basis sets at variational determination of interaction energy. The rectangles indicate the size of basis set; the dashed part indicate the occupied space.

$$\Delta E_C = E^{R\cdots T} - (E^{R(T)} + E^{T(R)}) \qquad (2)$$

$E^{R\cdots T}$ is the energy of the supersystem and $E^{R(T)}$ is the energy of subsystem R calculated within its "own" basis set as well as within the basis set of subsystem T. However, only atomic orbitals (and no electrons) are employed in the description of the subsystem T; these orbitals are therefore called "ghost" orbitals. The nuclear charges of all the atoms in this subsystem, T, are set equal to zero. Calculation of interaction energy by using eq 2 instead of eq 1 is more time-consuming; however, this increase is fortunately not too great because the two-electron integrals (whose calculation is the most time-consuming) are identical in the supersystem (R···T) and subsystems (R(T) and T(R)). For the subsystems R(T) and T(R), it is also necessary to calculate the one-electron integrals and to perform the SCF procedure.

The history of correcting the interaction energy for the BSSE is interesting. The very first application of the function counterpoise method was ill-advised; the method was used[11] for correcting the STO-3G interaction energies of some hydrogen-bonded systems. It was found that the calculated correction for BSSE is sys-

TABLE I. SCF Interaction Energies (ΔE) and SCF Interaction Energies Corrected for BSSE (ΔE_c) of Different Complexes (in kJ/mol)[a]

basis set	MINI-1		STO-3G		4-31G		6-31G*	
complex	$-\Delta E$	$-\Delta E_c$	$-\Delta E$	$-\Delta E_c$	$-\Delta E$	$-\Delta E_c$	$-\Delta E$	$-\Delta E_c$
$H_3N\cdots HF$	59.5	53.0	34.7	14.0	68.2		51.0	47.3
$H_2O\cdots HF$	48.2	39.6	31.4		65.5		38.5	
$(HF)_2$	29.2	17.9	23.0	−14.5	33.5	25.6	25.1	18.4
$(H_2O)_2$	28.1	20.1	25.0	−3.1	34.3	31.4	23.4	19.7
$OCO\cdots HF$	12.6	10.3	9.9	1.5	22.3	18.5	12.5	10.7
$(HCl)_2$	6.3	4.7	8.1	3.3	8.8	5.8	8.0	3.6

[a] Taken from ref 22. [b] Calculated at the potential energy minimum, evaluated with the specified basis set.

TABLE II. SCF Interaction Energies (ΔE^{SCF}), Correlation Interaction Energies (ΔE^{COR}), and the Respective BSSE and Total Interaction Energies (ΔE) Evaluated with Various Basis Sets for $(HF)_2$ and $(H_2O)_2$ (in kJ/mol)[a]

complex[b]	basis set[c]	$-\Delta E^{SCF}$	BSSE(SCF)	$-\Delta E^{COR}$	BSSE(COR)	$-\Delta E$
$(HF)_2$	6-31G* (0.8)	25.20	6.59	6.30	5.33	19.58
	6-31G* (0.25)	27.48	11.41	7.53	9.04	14.56
	6-31G** (0.8; 1.1)	24.98	6.40	5.80	5.34	19.04
	6-31G**′ (0.25; 0.15)	24.48	8.35	6.53	8.10	14.56
	6-311G** (1.75; 0.75)	21.42	4.52	4.05	4.47	16.48
	6-311G(d,2p) (1.75; 0.375, 1.5)	21.43	5.26	5.55	5.90	15.82
	6-311G(2d,2p) (0.875, 3.5; 0.375, 1.5)	20.84	4.65	6.01	5.00	17.20
	DZ+P (1.0; 1.0)	19.98	3.50	4.07	3.40	17.15
	DZ+P′ (0.25; 0.15)	21.83	5.94	5.50	6.77	14.62
$(H_2O)_2$	6-31G* (0.8)	23.35	3.78	6.39	4.48	21.48
	6-31G* (0.25)	23.44	7.35	7.77	7.21	16.65
	6-31G** (0.8; 1.1)	22.99	3.93	5.63	4.26	20.43
	6-31G**′ (0.25; 0.15)	23.06	6.66	8.05	7.18	17.27
	6-311G** (1.292; 0.75)	23.01	5.87	5.89	4.93	18.10
	6-311G(2d,p) (0.646, 2.584; 0.75)	22.09	6.00	7.23	4.82	18.50
	DZ+P (1.0; 1.0)	20.44	2.93	5.06	3.55	19.02
	DZ+P′ (0.25; 0.15)	21.31	5.62	9.45	8.40	16.74

[a] Taken from ref 25. [b] Geometry taken from SCF optimization with 6-31G*. [c] Exponents of polarization functions are given in parentheses.

tematically too large and the authors[11] ascribed this overestimation to the nature of function counterpoise method. It was shown later[12-14] that this overestimation was due to the STO-3G basis set and not to the counterpoise method. Nevertheless the idea persisted that the function counterpoise method overcorrected the basis set extension effect and some reductions of the BSSE were proposed. It was suggested that a damping factor[11,15,16] be used, or that the BSSE be calculated with only the virtual orbitals of the "ghost" subsystem[17,18] or even only with the polarization functions of this subsystem.[19] In 1977 T. P. Groen and F. B. van Duijneveldt demonstrated[20] theoretically that the full rather than reduced BSSE must be included. Unfortunately these results have never been published. In the late 1970s and at the beginning of the 1980s, it was almost generally accepted that inclusion of the (full) counterpoise correction brings the interaction energy evaluated with any basis set (except STO-3G; see the discussion in ref 21) closer to the respective Hartree–Fock limit. Table I gives some typical examples: the BSSE is usually small (except for STO-3G) and extension of the basis set reduces its value. It was expected that, with very large basis sets (which are close to the HF limit), the BSSE will be negligible. An example is the calculation for $(H_2O)_2$. With the [432|21] basis set,[13] the SCF interaction energy and BSSE amount to −16.19 and 0.63 kJ/mol. With larger [8521|421] basis set,[23] the SCF interaction energy equals −16.32 kJ/mol and the BSSE was estimated[13] to be less than 0.21 kJ/mol. Alagona et al.[24] investigated nine hydrogen-bonded complexes with five different basis sets. Their findings on the BSSE are in full accord with the above-mentioned conclusions. A study by Schwenke and Truhlar,[19] which disagrees with this conclusion, should be mentioned here. The authors[19] studied the $(HF)_2$ dimer and found that inclusion of the BSSE does not improve the accuracy obtained with different basis sets. We believe that the main difficulty was due to the fact that only one of the basis set dependent quantities (BSSE) was corrected. The second quantity, the dipole moment, is very much sensitive to the basis set. Only after correcting both the dipole moment and BSSE can a systematic improvement be expected in the accuracy of ΔE^{SCF}.

The situation has changed since beyond Hartree–Fock methods were used for evaluation of correlation interaction energy. It soon became evident that, in order to obtain a high percentage of electron correlation, the basis set must contain very diffuse (flat) polarization functions (see below). The correlation interaction energy increases considerably if these functions are included; on the other hand, unfortunately, the magnitude of the BSSE also increases. If the basis set contains flat functions, the BSSE is not negligible, even for large basis sets; the situation is even more serious with beyond Hartree–Fock energies. Here the BSSE is frequently comparable to ΔE^{COR} or is even larger,[25-28] and this is true even with extended basis sets (DZ+P and larger). Some typical examples are given in Table II. This may, of course, incite some doubts about the applicability of the function counterpoise procedure in general or, at least, with beyond Hartree–Fock energies.

However, convincing evidence was recently obtained,[29-31] showing that the "full" counterpoise correction should be employed at both the SCF and beyond SCF levels. On the basis of a detailed analysis of the perturbation first-order and higher order components of the interaction energy for $(He)_2$ and $He \cdots Li^+$, it was demonstrated that the frequently used objection against the use of the full counterpoise correction, based on the supposed violation of the Pauli principle, is not valid. On the contrary, evidence was obtained that the whole dimer basis set is available for the monomers. In ref 32, other objections to the use of the full counterpoise correction[33] are shown to be unjustified. Numerical data for $(He)_2$ and $(H_2)_2$, collected in papers 34 and 35, demonstrate that neglecting the BSSE would result in overestimated interaction energies, larger than the experimental value (for $(He)_2$) or larger than the reference theoretical value (for $(H_2)_2$). We would like to comment on the recommendation by Frisch et al.[6] to neglect the BSSE. The authors[6] compared the theoretical and experimental ΔH value for the formation of the $(H_2O)_2$ dimer. On the basis of a close agreement between uncorrected ΔH_{373} and the respective experimental value (−15.1 and −15.5 kJ/mol), the authors[6] concluded that it was not necessary to consider the BSSE. The agreement is really close but two facts have to be kept in mind. First, the experimental value is connected with a rather large error, the actual value[4] is −15.5 ± 2.1 kJ/mol. Second, despite the inclusion of higher polarization functions (6-311G++ (3df,3pd)), the basis set is still not saturated with respect to the evaluation of ΔE^{COR} (especially because the standard and not diffuse f and d functions were used). Let us demonstrate this situation with use of the results of three recent papers. For $(Be)_2$ it was found[36] that an spd basis set can only account for two-thirds of the accurate interaction energy. Addition of a diffuse set of f functions ($\alpha_f = 0.4$) leads to an important increase of interaction energy. Very similar results for the efficiency of spd basis set were found[26] for $(Mg)_2$. Addition of diffuse f functions ($\alpha_f = 0.14$) leads to an important increase in the interaction energy (by more than 20%); if more concentrate f functions ($\alpha_f = 1.4$) are added to the spd set, a much smaller increase resulted (less than 10%). Finally, the results concerning $(Ne)_2$ will be mentioned.[37] The spd set is again too small to provide an accurate value of the interaction energy, addition of the diffuse f functions increases the interaction energy by about 10%, and a further increase by about 5% results from inclusion of the g functions. In the light of the above arguments, larger value of ΔH (compared with that reported in ref 6) would result if a larger, carefully selected basis set were employed. Any estimation of the truncation error is difficult but a value of 2 kJ/mol seems to be reasonable. The uncorrected ΔH, with inclusion of this error is −17.1 kJ/mol, while the BSSE corrected ΔH is −14.1 kJ/mol. Clearly, both values fit into the experimental range. Hence, the results of paper 6 are not suitable enough for deciding on the usefulness of correction for the BSSE.

It seems desirable to take the BSSE into account at the SCF level, because the BSSE for good basis sets is significantly smaller than ΔE^{SCF}. If the BSSE is comparable to or even larger than ΔE^{SCF}, the respective basis set cannot be recommended. This happens only with some minimal basis sets, e.g., with STO-3G. The situation is less clear at the beyond SCF level. In this case, the BSSE(COR) is comparable to ΔE^{COR} even for rather extended basis sets, and is sometimes even larger than ΔE itself. In the latter case, ΔE^{COR} is repulsive. Does such a result have any physical basis? The answer is yes, and moreover this is an important argument for taking the (full) counterpoise correction into account. Let us briefly comment on the results of paper 28. At larger subsystem distances in the "linear" $(H_2O)_2$ complex, repulsive values of ΔE_c^{COR} were obtained, even with an extended basis set. On the basis of a detailed analysis of the perturbation components of ΔE^{COR}, it was shown that, at these distances, the change in the intrasystem correlation energy is positive and, furthermore, that its absolute value is larger than the (negative) intersystem correlation energy. Thus, the total ΔE^{COR} should be positive at large distances. This is not surprising, because the intersystem correlation energy (negative) decays with the sixth power of the reciprocal distance. In this case, a change in the intrasystem energy results basically from the term containing the product of the difference of the SCF and the correlated dipole moments of both subsystems; this term, which is positive for the linear structure of $(H_2O)_2$, decays with the third power of the reciprocal distance. If the BSSE is not fully taken into account, a physically incorrect—negative—ΔE^{COR} results. For larger, more polarizable systems, the change in the intrasystem correlation energy will have a smaller absolute value than the intersystem correlation energy. The former contribution may reduce the latter by as much as 20%.

Evidence was presented above that indicates that it is desirable to correct ΔE^{SCF} as well as ΔE^{COR} for the respective BSSE. How should we interpret the values in Table II? It is seen that ΔE_c^{COR} for $(HF)_2$ is very small and is repulsive for the majority of the basis sets. For $(H_2O)_2$ ΔE_c^{COR} is negative, but rather small. Evidently, in both cases the change in the intrasystem correlation energy is repulsive, making the resulting ΔE_c^{COR} small or repulsive. This is, in both cases, physically correct. The obtained values of ΔE^{COR}, however, represent the lower limit of the real correlation contribution, because the basis sets given in Table II are too small to yield accurate values of ΔE^{COR}. As will be seen later, the inclusion of higher polarization functions is inevitable. Corrected values of ΔE^{COR}, evaluated by using currently available basis sets, are lower than the real values of ΔE^{COR}. It is therefore tempting not to correct the ΔE^{COR} (evaluated with medium basis sets) for the BSSE. This approach cannot be recommended because the lower limit to ΔE^{COR} will not be obtained but instead some overestimated value of ΔE^{COR}. Then it would not be possible to estimate whether the value of ΔE^{COR} obtained approaches the real value from above or below.

The interaction energy evaluated by using the Hartree–Fock method and any beyond Hartree–Fock method (provided it is size-consistent) should be corrected for the BSSE at both levels. For medium-sized complexes, where one is able to work with only medium basis sets (DZ+P type), the calculated value of ΔE_c^{COR} represents the lower limit of the real correlation interaction energy. If the BSSE were not taken into account, a physically uncorrect interaction energy could be obtained.

So far, it has been assumed that the geometry of subsystems remains rigid and only the intersystem coordinates are optimized. In such a case, the function counterpoise method can be applied in a straightforward way. With stronger vdW molecules, e.g., H-bonded complexes, the intrasystem coordinates should also be optimized. It is now more tedious[30] to correct for the BSSE: first, it is necessary to evaluate the corrected interaction energy for the distorted geometry (the geometry of the subsystems is changed); further, the deformation energies of both the subsystems must be evaluated, and, finally, the total corrected interaction energy is constructed as the sum of all three contributions. From the point of view of calculation of the energy hypersurface (where the intrasystem geometry must be optimized) it would be desirable to work with basis sets having a small BSSE or with procedures completely avoiding the BSSE; in these cases it would be possible to avoid tedious correction for the BSSE at each point on the hypersurface. Let us first discuss the former possibility. Huzinaga's basis sets,[38] constructed to reduce the BSSE, can be recommended. It must be kept in mind, however, that even with these basis sets the BSSE is not negligible. Another approach involves reoptimization and modification of the standard basis sets to reduce the BSSE. We are not fond of this approach, as reoptimization of the basis set, leading to a decrease in the BSSE, usually leads to magnification of some other, unfavorable property. The pertinent papers will be described for the sake of completeness. Kołos demonstrated[39] several years ago that the value of the BSSE for some minimal basis sets is reduced by reoptimizing the exponents of the hydrogen atoms. This idea was recently extended in papers 40 and 41. The authors have studied a large number of modifications to the standard 6-31G** basis set; the most efficient involves reoptimization of the orbital exponents within the framework of the relevant molecule and addition of a single diffuse shell of sp orbitals to nonhydrogen atoms. The other possibility, i.e., to work with procedures avoiding the BSSE completely is very tempting. Recently two papers appeared[42,43] in which the interaction energy was evaluated within a perturbation method; the use of second quantization and bi-orthogonal techniques ensure elimination of the BSSE without any a posteriori correction. The technique has also been applied to the variation approach[44] and specific SCF–LCAO–MO type equations were derived, permitting supermolecular calculations of the interaction energy by avoiding the BSSE from the very beginning. These methods can be conclusively evaluated only on the basis of more extensive numerical data.

It was pointed out[45] that evaluation of corrected interaction energy by means of the counterpoise method may be complicated by the fact that the introduction of "ghost" functions lowers symmetry of the wave function.

2. Size-Consistency Error

The configuration interaction method including all the singly and doubly excited configurations (CI-SD) is an efficient method for evaluation of the correlation energy and covers a significant portion thereof. Furthermore, because it is a genuine variation method, it furnishes an upper bound to the energy. A drawback of the method (similarly to CI-D), which prevents its broader use in the field of molecular interactions, is the incorrect dependence on the number of particles, called the size-consistency error.[45a] In the language of molecular interactions, this means that the energy of the supersystem evaluated for an infinite inter-subsystem distance should be equivalent to the energy of the two isolated subsystems. The size-consistency error should be eliminated, as this error can be as large as the stabilization energy itself. The rigorous elimination of the size-consistency error requires the inclusion of quadruply excited configurations (CI-SDQ). This, however, increases the computational time enormously. Another possibility is not to use a size-inconsistent method. If neither of these possibilities is acceptable, the error can be partially eliminated by determining the interaction energy using eq 3, where $E^{\mathrm{R\cdots T}}(r)$ and $E^{\mathrm{R\cdots T}}(\infty)$ are the

$$\Delta E = E^{\mathrm{R\cdots T}}(r) - E^{\mathrm{R\cdots T}}(\infty) \qquad (3)$$

energies of the complex at distance r and at a very large distance (e.g., 100 au). Let us add that the size consistency error is not eliminated completely in this way, as this error is not the same at distance r and at a large distance. Therefore, some empirical correction procedures have been suggested, the most popular of which are those of Davidson[46] and Pople;[47] if the respective corrections are added to each energy in eq 3, we may hope to eliminate the error. An example is data for $(H_2O)_2$,[48] obtained by using the CI-SD method with an extended basis set. If the interaction energy is evaluated by means of eq 1 (the standard way), a repulsive ΔE results (34.8 kJ/mol). Taking the size-consistency error into account (eq 3), the stabilization of −20.7 kJ/mol is obtained, and finally, if the Pople correction is employed in combination with eq 3, the stabilization energy amounts to −21.1 kJ/mol. Evidently, the size consistency error is enormous for this dimer (about 55 kJ/mol). Similar evidence for the importance of the size-consistency error was obtained for $(Be)_2$. It is very instructive to compare the CI calculations carried out[49] at different levels for a single basis set ([7s3p1d]). While the CI-SDTQ calculation (considering only four valence electrons) predicts a minimum of 2.93 kJ/mol at 265 pm, the CI-SD calculation yields a very shallow minimum at 450 pm. Correction of the values obtained by the CI-SD calculation by the Davidson method yielded a very shallow minimum at 450 pm and a deep minimum of 4.6 kJ/mol at 265 pm.

The size inconsistency clearly limits the use of the CI-D and CI-SD methods. Recently a size-consistent modification of the CI-D method was developed[50] and applied to $(NH_3)_2$[51] and $H_2O\cdots Mg$[52] complexes. The modification is based on an energy functional and is called the coupled pair functional method.

3. Selection of Basis Sets

The choice of a basis set is affected by two very different requirements. First, the basis set should be kept within reasonable limits because of the notorious n^4 catastrophy, and second, the selected basis set should describe the complex as accurately as possible. Within the framework of classical quantum chemistry, the calculations must attain what is called "chemical accuracy", i.e., must not differ, roughly speaking, by more than 0.001 hartree from the accurate value. One millihartree is about 3 kJ/mol, which is comparable to or even more than the stabilization energy of a great

TABLE III. Dipole Moments[a] of H_2O and HF Given by Different Basis Sets[b]

	STO-3G	MINI-1	[2s1p/1s]	4-31G	DZ	6-31G*	DZP	DZPP	HF limit
H_2O	6.2	7.5	7.3	8.3	9.0	7.3			6.7
HF	4.2	6.6		7.6	8.0	6.6	6.9	6.5	6.5

[a] In 10^{-30} C m. [b] From ref 22, 53, 54.

many true vdW molecules. For some vdW molecules a higher accuracy is necessary. It is more practical to introduce some relative measure of accuracy. Applying the 10% limit of accuracy would imply calculation of the stabilization energy of true vdW molecules with accuracy of about 0.01–0.1 kJ/mol and that of H-bonded complexes with accuracy 0.5–1 kJ/mol. This is a very difficult task and is still hardly feasible in routine calculations. Before speaking about the choice of basis set in detail, let us mention one example documenting how difficult it is to obtain accurate values. The dispersion energy of $(Ne)_2$ was evaluated[37] with s, p, d, f, g, and h AO's. If the basis set contains s, p, and d AO's, then the dispersion energy recovered represents 72–84% (depending on the distance) of the total dispersion energy; a basis set containing s, p, d, and f orbitals yields 92.5–96.7%, and if the g orbitals are included, 98.1–99.2% of the total dispersion energy is obtained. This example again creates a feeling of hopelessness, as a dispersion energy value with an error of less than 10% can be obtained only by including the f orbitals of the particular vdW molecule. It seems that with polyatomic systems (with more than about 10 atoms) these extreme requirements are not valid and satisfactory description can be obtained with less extensive basis sets. This is due to higher flexibility of the wave functions of polyatomic systems.[52a] The $(Ne)_2$ dimer belongs among true vdW molecules, where the whole stabilization comes from the dispersion energy; with H-bonded complexes an important part of stabilization originates from the HF interaction energy. Evaluation of the accurate values of the HF interaction energy is much easier than for the dispersion energy.

How can we rationalize the choice of the basis set? Is it necessary to test the basis set for interaction energies or is there any other easier (cheaper) selection procedure? In the previous part, it was pointed out that the interaction energies evaluated by variation and perturbation procedures are equivalent. The HF interaction energy is approximately equivalent to the sum of the Coulombic, induction, and exchange-repulsion energies, while the correlation interaction energy can be, at large intersystem distances, identified with the dispersion energy. The Coulombic energy represents frequently the major contribution to the ΔE^{HF} value. This term is proportional to the multipoles of both the subsystems. The induction energy is proportional to the multipoles of one subsystem and the polarizability of the second subsystem. Clearly the multipoles of both the subsystems are very important quantities for determination of ΔE^{HF}. If the basis set in question is not able to properly describe the multipole moments of the subsystems, then it cannot correctly describe ΔE^{SCF}. Table III gives the dependence of the dipole moments of H_2O and HF on the basis set. It can be seen that the minimal basis sets yield values that are rather similar to the Hartree–Fock limit. This agreement is, however, fortuitous; enlarging the basis set leads to an increase in the dipole moment. Only after addition of the polarization functions is the requirement of 10% agreement with the HF limit obtained. It follows from the table that the presence of polarization functions is inevitable in order to obtain an accurate ΔE^{HF} value. Let us add that a 10% error in the dipole moments creates about a 20% error in the SCF interaction energy. To obtain a 10% error in the interaction energy, the dipole moment must be calculated more accurately, which requires addition of a second set of polarization functions. It also follows from Table III that minimal basis sets can yield surprisingly reasonable values of ΔE^{SCF}, better than those obtained with a DZ basis set. This result is evidently due to the compensation of errors, but nevertheless appears promising for calculation of ΔE^{SCF} for large vdW molecules. So far we have mentioned only dipole moments. In molecules with quadrupole moments, the situation is more complex. An accurate calculation of the dipole moment requires inclusion of the first polarization functions in the basis set and accurate evaluation of quadrupole moment requires that the basis set be augmented by higher polarization functions. For example, for the H_2 and N_2 molecules, the d and f functions, respectively, should be included.

For polar systems, multipole moments can be used for testing the reliability of basis sets for evaluation of ΔE^{SCF} in the region where the Coulombic energy is dominant. This is long-range region and the region of the vdW minimum. In the repulsion region the exchange-repulsion term is dominant. If this part of the potential energy curve is being studied (which is, however, not common), further criterion for basis set selection should be applied. It has been shown[55] on the basis of analysis of the perturbation exchange-repulsion term that the overlap of valence AO plays the dominant role. The basis set should therefore correctly describe this overlap for all intersystem distances. The standard basis sets are energy optimized; these basis sets yield wave functions that are satisfactory near the atoms but poor for farther distances. The requirement for proper evaluation of the exchange-repulsion energy (and hence also of ΔE^{SCF} in the repulsion region) is the correct description of the valence orbitals in regions other than in the closest vicinity of the nuclei; the quality of the inner-most orbitals can be lower.[55,56]

In the previous part we have seen that the choice of the basis set for accurate evaluation of ΔE^{SCF} is not too difficult. With a carefully chosen DZ+P basis set, the 10% limit to ΔE^{HF} can be approached. When selecting the exponent of the polarization functions, the following standard exponents can be recommended:[53] $\alpha_p^H \sim 1.0$; $\alpha_d^{C,N,O,F} \sim 1.0$; $\alpha_d^{P,S,Cl} \sim 0.5$. These (or similar) exponents are used in the widely employed standard Dunning's DZ+P or Pople's 6-31G** basis sets. The exponents of the second set of polarization functions (DZ+2P or 6-311G(2d,2p) basis sets) are far more diffuse. Before concluding, it should be noted in this connection that, with a carefully prepared minimal basis sets, a reasonable ΔE^{SCF} value can be obtained.

The selection of a basis set for the second part of the total interaction energy, the correlation interaction energy, is more complicated. First, there is no chance at all of obtaining quantitatively correct values of ΔE^{COR} with small basis sets (minimal and DZ). The ΔE^{COR} value found with these basis sets can be considerably underestimated. For the stacking $(H_2O)_2$ dimer, the relative ΔE^{COR} value (compared to ΔE^{COR} evaluated with STO-3G) determined with MINI-1, 4-31G, 6-31G*, and DZ+2P amounts to[57] 1, 2.4, 2.7, and 6.5. With more polarizable molecules, the underestimation of ΔE^{COR} when small basis sets are used can be larger[57] (1 order of magnitude or more). Let us analyze the role of different types of polarization functions with $(He)_2$.[58] The effect of inclusion of f-type functions is rather small and corresponds to about 2% of the total correlation interaction energy at the potential minimum. The contribution of d-type functions is larger (~20%) but still not decisive. The largest part of the correlation interaction energy (about 75%) is due to the first polarization functions, i.e., the p-type functions for $(He)_2$. The effect of g-type functions (localized on H_2 or He) has been studied for the He···H_2 complex.[59,60] It was found that these functions contribute less than 1% to the intersystem correlation energy at the potential minimum. Extending the basis set by inclusion of other d- or f-type functions has a small effect. The following increase in the polarization space was recommended[8] for $(He)_2$: 1p, 1p1d, 2p1d1f, 2p1d1f1g, 3p2d1f1g1h. This set should serve as a guideline rather than as a strict prescription. For the $(H_2)_2$ dimer,[35] the following string of polarization functions were found: 1p, 2p, 3p, 2p1d, 3p1d. In both cases,[8,35] the sequence of basis is affected by the fact that superposition of basis sets was taken into account. The order of higher polarization functions can be different for various vdW molecules: the very beginning of the string is, however, always the same. The first polarization functions play a dominant role in the calculation of the ΔE^{COR}. The contribution of the higher polarization functions is less important. If, however, accurate calculations of the interaction energy are to be carried out, higher polarization functions, especially the second functions (the f type for Li–Ne and the d type for H and He), must then be included. The importance of the first and second polarization functions is not surprising. It was shown at the beginning of this paragraph that ΔE^{COR} at large distances basically consists of the dispersion energy. The expanded dispersion energy is evaluated as the sum of contributions proportional to r^{-6}, r^{-8}, r^{-10}, r^{-12}, ... The first term contains the product of dipole polarizabilities, and the second and third term contain the product of the dipole and quadrupole polarizabilities and the product of quadrupole polarizabilities, respectively. The sum of the second and third term corresponds to at least 10–15% of the total dispersion energy. It has long been known[54] that proper evaluation of the dipole and quadrupole polarizabilities requires inclusion of the first and second polarization functions, respectively; these functions must be sufficiently diffuse. Optimizing[54] the DZ+2P basis with respect to the dipole polarizabilities of different molecules yields the following values for the exponents of the diffuse set of polarization functions: $\alpha_d^{C,N,O,F} = 0.15$, $\alpha_p^H = 0.08$. The DZ+2P basis set gives quite accurate values of the dipole polarizabilities and dipole moments. This basis set can therefore be recommended for calculation of the interaction energy between dipolar subsystems containing atoms of the first-row elements. For those who prefer to work with some standard basis sets of the GAUSSIAN program series (e.g., GAUSSIAN 82),[61] the 6-311G (2d,2p) basis[62] set can be recommended (6-311G is approximatively equivalent to (9s5p)). The exponents of the d and p types of polarization functions were obtained from the original set with a single polarization function (within the 6-311G**) by multiplying the exponents of the original set by $^1/_2$ (leading to more diffuse functions) and by 2 (functions centered on the atoms). The exponents of the diffuse functions obtained in this way amount to the following: H, He 0.375, Li 0.10, Be 0.128, B 0.201, C 0.313, N 0.457, O 0.646, F 0.875, and Ne 1.152. The exponents for diffuse polarization functions for H, C, N, O, and F presented above in connection with DZ+2P basis set are, however, smaller. The ΔE^{COR} evaluated with the 6-311G (2d,2p) basis set may be underestimated. It was already mentioned that accurate values of dispersion energy are obtained only if higher polarization functions are taken into account, i.e., to include f functions with the first-row elements and *d* functions with hydrogen. These functions should be again much more diffuse (almost by 1 order of magnitude than those obtained from energy optimization). The following values were obtained by optimization of the subsystem quadrupole polarizability or of the interaction energy of vdW molecule: α_f^{Be} 0.4,[36] α_f^O 0.18,[63] α_f^F 0.275,[64] α_f^{Ne} 0.28,[65] α_f^{Mg} 0.14,[26] α_d^H 0.075.[64] Neglection of higher polarization functions or using the energy-optimized exponents in these function results in underestimation of the quadrupole polarizability and, consequently, in underestimation of the dispersion energy by 10–15%.

The exponents of the polarization functions can be optimized with respect to a property of the subsystem (the polarizability) or of the supersystem (ΔE^{COR}, E^D). The values given above were mostly based on optimization of the dipole or quadrupole polarizabilities. Optimization based on, e.g., the dispersion energy has the advantage that not only the first terms of the dispersion energy expansion but also the higher terms are included. It would be preferable to optimize those exponents with respect to ΔE^{COR}. The optimization for the individual vdW molecules (usually for the distance of the expected vdW minimum) would be very expensive and tedious. Fortunately, it was found[66] that the exponents for the AO's of a given atom in subsystem R, determined by optimization of ΔE^{COR} or E^D in the R···R vdW molecule, can also be used for the R···T vdW molecule. Unfortunately, sufficiently complete and consistent optimization of the exponents of the polarization functions of various atoms has not yet been carried out with ΔE^{COR}. However, a related study has been performed with the dispersion energy.[66] As the dispersion energy constitutes a major part of the intersystem correlation energy, the results of this study can also be used for ΔE^{COR}. Table IV lists the optimized values of the exponents of the polarization functions for the atoms of various elements. The exponents given in Table IV can be compared with recommended values listed above. The exponents in Table IV are suitable for evaluation of E^D or ΔE^{COR} but not for

TABLE IV. The Exponents of the Polarization Functions Obtained by Optimization of the Dispersion Energy[a]

atom	H	He	Li^+	Li	Be[b]	B[b]	C	N[b]	O	F[b]	
p-type function	0.2	0.3	0.775	0.04							
d-type function		0.14		0.035	0.08	0.12	0.17	0.225	0.287	0.36	
atom	Ne	Mg^{2+}	Mg^+	Mg	Cl	Ar	Ca^{2+}	Ca^+	Ca	Br	J
p-type function			0.138	0.12				0.09	0.08		
d-type function	0.45	1.02	0.17	0.15	0.22	0.28	0.56	0.17	0.11	0.15	0.14

[a] Reference 66. [b] The values were obtained by the extrapolation of the dependence of the polarization function exponents for the Li, C, Na, and Ne atoms on the atomic number.

evaluation of ΔE^{SCF}. In order to correctly calculate the total interaction energy, two sets of polarization functions must be used: a diffuse set (exponents taken from Table IV) and a set concentrated on the atoms (for the respective exponents, see the previous part). Such a basis set (DZ+2P) gives accurate values of the interaction energy but is prohibitively large for more extended vdW molecules. With such a molecule, only the DZ+P basis set can be used. How should the polarization functions be selected in this case? Compromise sets of polarization functions were proposed in ref 54. The authors[54] have optimized the exponents of the polarization functions for the DZ+P basis set with respect to the dipole moment and dipole polarizability of different molecules. The exponents obtained are as follows: $\alpha_p^H = 0.15$, $\alpha_d^{C,N,O,F} = 0.25$. Let us now investigate the quality of this basis set in comparison with similar basis sets. Table II lists the energy characteristics based on the compromise basis sets (6-31G*′, 6-31G**′, DZ+P′) as well as on the original basis sets for $(H_2O)_2$ and $(HF)_2$. ΔE^{COR} and BSSE(COR) are larger for both complexes with compromise basis sets than those obtained with the original basis set; ΔE_c^{COR} is, on the other hand, smaller when the compromise basis sets are used and is even repulsive for $(HF)_2$. Are these results physically correct? The way of answering this question is to compare the respective results with those obtained with extended basis sets. The required data are available only for the $(H_2O)_2$ dimer. The following values of ΔE, corrected for both BSSE's, were obtained[48] by the SD-CI method (size inconsistency was corrected by means of the Pople method) with the following basis sets DZ+P′, DZ+2P, EZ+2P (EZ is extended ζ): −16.61, −16.90, and −17.11 kJ/mol, respectively. Very similar values are found in Table II for DZ+P, 6-31G*′, and 6-31G**′ basis sets (the MP2 method is used throughout the table for evaluation of ΔE^{COR}), while the other (standard) basis sets in Table II yield larger values of ΔE_c. For $(HF)_2$, the ΔE_c values evaluated with compromise basis sets are again smaller than those evaluated with the corresponding standard basis sets. In spite of the fact that values obtained with extended basis sets are lacking for this dimer, we believe that compromise basis sets yield more reliable interaction energies (compared with the respective standard basis sets) even for this dimer.

The above results demonstrate the importance of the polarization functions for accurate evaluation of ΔE^{COR} as well as for accurate calculation of the total interaction energy. The presence of two sets of first polarization functions and one set of second polarization functions is necessary for the results to be close to the accurate interaction energy. Surprisingly reasonable values of the interaction energy for H-bonded complexes are obtained even with a basis set containing only one set of polarization functions; the respective exponents should be optimized simultaneously with respect to the dipole moment and dipole polarizability. Smaller basis sets than DZ+P yield underestimated ΔE^{COR} values and, consequently, physically incorrect interaction energy. This is, of course, true only if ΔE^{COR} is calculated with these basis sets. If ΔE^{COR} is evaluated in another way, then reasonable ΔE^{SCF} values can be obtained already with properly chosen minimal basis sets. We must pay attention to the superposition errors of these basis sets. From this point of view the use of the popular STO-3G basis set is not recommended (see Table I). On the other hand, Huzinaga's minimal basis set MINI-1[21] seems to be very useful. This basis set was prepared so as to minimize the BSSE value. After the respective ΔE^{SCF} is corrected for the BSSE, good agreement is obtained with the interaction energy evaluated for the DZ+P basis set (see Table I). This is true not only for neutral vdW molecules but also for ionic vdW species of the $X^+\cdots M$ and $X^-\cdots M$ (M is a molecule) types.

4. Effect of Single, Double, Triple, and Quadruple Electron Excitations

The total correlation interaction energy consists of three contributions: the intersystem correlation energy, the change in the intrasystem correlation energy, and the coupling term between them. Calculating the individual terms requires localization of the orbitals. Our aim is to calculate the correlation interaction energy for the R···T vdW molecule, where both subsystems have completely occupied bonding orbitals. The classical approach is to use the configuration interaction (CI) treatment. Although the CI method is impractical for routine calculations, it is advantageous to use it to explain the role of different types of excited configurations. We need to know the role of singly, doubly, triply, and quadruply excited configurations in the CI expansion. The main contribution to the correlation energy of isolated system (more than 90%) comes[53] from the doubly excited states. What is the role of these excitations in vdW molecules? The doubly excited configurations make a major contribution to ΔE^{COR}. There are two main types of double excitations. First, both electrons originate from one subsystem and both pass together to the virtual space of either subsystem. Second, one electron originates from each subsystem and, after excitation, either of the virtual space contains an electron. In the former case, the intrasystem correlation energy of one subsystem is modified by the presence of the second subsystem, while in the latter case intersystem correlation energy arises. While the change in the intrasystem correlation energy may be repulsive or attractive, the intersystem correlation energy is always attractive and corresponds to the nonexpanded dispersion energy and exchange dispersion energy. With isolated molecules, the second most important contribution to the correlation energy comes from unlinked quadruple excitations, followed by contributions originating in triple and single excitations.[53] The importance of these excitations differs for vdW molecules. In this case, the second most important contribution (after double excitations) comes from triple excitations. Three electrons should be excited in such a way that two electrons originate from one subsystem and one from the other subsystem; after excitation each virtual space contains at least one electron. This excitation leads to the formation of the coupling term between the intersystem and intrasystem correlation energies. The single and quadruple excitations are less important for vdW molecules; they cannot, however, be neglected in the most accurate calculations. The effect of singly excited configurations is small, as described by Brillouin's theorem. These considerations are, however, connected with energy predictions. With other characteristics, these configurations may play an important role. Let us mention, as an example, the dipole moment of CO. The HF dipole moment has the wrong sign; the inclusion of singly excited configurations in the CI expansion leads to the correct sign of the dipole moment.[67] Clearly, the HF calculations as well as, e.g., CI-D calculations should fail in prediction of the structure and energy of complexes containing the CO molecule; only after addition of the singly excited configurations can reasonable characteristics be obtained for these complexes.

In order to describe all the components of the correlation interaction energy, it is necessary to include doubly and triply excited configurations; singly and quadruply excited configurations may also (indirectly) play an important role in evaluation of the interaction energy. Hence, only methods including single, double, triple, and quadruple excitations can succeed in accurate prediction of different characteristics of vdW molecules. Let us analyze the different theoretical methods in this light. Obviously, the CI-SDTQ method represents the reference method. Unfortunately, the cost of such calculations is enormous and they have been carried out only for a very few vdW molecules. An example is the calculation of the interaction energy of $(H_2)_2$;[49] a single point for the dimer (with 78 basis functions) required 8 h of CPU time on CRAY-1. How can the CI treatment be made feasible for larger vdW molecules? Unfortunately, this is impossible, because reducing the extent of CI by neglecting some types of excitations would lead to a loss in either the size consistency (for quadruple excitations) or the accuracy (for triple excitations).

The many-body perturbation treatment (MBPT) seems very promising from the point of view of accuracy and economy. The form in which it is mostly used is connected with special partitioning of the Hamiltonian due to Møller and Plesset.[68] Therefore, the abbreviation MP is also used. In order to include all the above-mentioned excitations it is necessary to perform the calculation through the fourth order. The correlation interaction energy is determined as a sum of the second-, third-, and fourth-order contributions

$$\Delta E^{\mathrm{COR}} = \Delta E^2_{\mathrm{D}} + \Delta E^3_{\mathrm{D}} + \Delta E^4_{\mathrm{S}} + \Delta E^4_{\mathrm{D}} + \Delta E^4_{\mathrm{T}} + \Delta E^4_{\mathrm{Q}} \quad (4)$$

where the superscript refers to the order of the perturbation calculation while the subscript refers to the type of excitation. The second- and third-order contributions consist of double excitations alone, while single, double, triple, and quadruple excitations appear in the fourth order. The first question that must be answered is how fast the perturbation expansion converges, i.e., whether it is possible to truncate the perturbation expansion at the fourth order. The convergence of the perturbation expansion for $(Be)_2$ up to the eighth order was studied in paper 69; the perturbation energies were calculated by using an adapted CI program. The values (in kJ/mol) of the second-, third-, fourth-, fifth-, sixth-, seventh-, and eighth-order perturbation energies, determined at the vdW minimum, are as follows: −5.454, −0.561, −0.261, 0.031, 0.033, 0.029, and 0.011. The energies evidently become smaller after the fourth-order term; the fourth-order energy is larger than the sum of the remaining terms in the perturbation series. It is apparent, however, that the expansion converges slowly. Similar conclusion on the convergence of the MBPT expansion for $(Be)_2$ were drawn in ref 70. The results presented above support an approach that is now widely used, i.e., to truncate the MBPT expansion after the fourth order.

The quality and economy of MBPT calculations performed through the fourth-order require comment. The SDTQ-CI calculation for the $(H_2)_2$ dimer (T structure, R = 3.44 Å) with [4s3p, 1s1p, 1d] basis set yields[49] an interaction energy value of −433 J/mol. For a slightly different distance in the same structure (R = 3.66 Å), the following value of the interaction energy evaluated at the MP4 level with the same basis set was found:[35] −393 J/mol. The potential curve for the T structure of the $(H_2)_2$ dimer is very flat[71] in the region of distances for which the above-mentioned calculations were carried out; the interaction energies differ in this region by not more than 10 J/mol. Adding this value to ΔE^{MP4} leads to an interaction energy of about −403 J/mol. The difference between $\Delta E^{\mathrm{MP4}}_{\mathrm{EST}}$ and ΔE^{CI} is rather small (ca. 30 J/mol or about 7%), which can be attributed to the inclusion of higher order contributions. The CI calculation took 8 h[49] on CRAY-1, while MP4 required only 5.3 h[35] on VAX 780. This comparison strongly favors the use of the many-body perturbation treatment through the fourth order.

The relative importance of the second-, third-, and fourth-order contributions should also be mentioned. The data given above for $(Be)_2$ are typical: the second-order term is by far the most important contribution; the third- and fourth-order terms are less important. Table V contains the data for different vdW molecules. From this table it becomes clear that ΔE^2 is dominant for all the different types of vdW molecules, ΔE^3 is, however, by no means negligible. The latter term is sometimes negative and sometimes positive but, evidently, there is no rule governing the sign. The fourth-order term always has an absolute value smaller than that of the third-order term; ΔE^4 is sometimes important and sometimes negligible. Again, it is impossible to ascribe the compensation to some special type of vdW molecules. The role of triple excitations at the fourth-order level is worth mentioning. From Table V it is clear that this contribution forms an important or even dominant part of the ΔE^4 term. Neglecting triple excitations completely results in unrealistic

TABLE V. The Second- (ΔE^2), Third- (ΔE^3), and Fourth- (ΔE^4) Order Contributions to the Correlation Interaction Energy and Contribution to the Fourth-Order Term Coming from Triple Excitations (ΔE^4_T) for Different vdW Molecules Calculated at the vdW Minimum; Values in the Second Line Were Corrected for the Basis Set Superposition Error (Energies Given in J/mol)

vdW molecule	basis set	ΔE^2	ΔE^3	ΔE^4	ΔE^4_T	ref
$(He)_2$	[7s4p3d]	−132				34
		−121	−20	−7	−7	
$(Mg)_2$	[7s4p2d1f]	−12636	−1586	−462	−888	72
$(Ar)_2$	[7s4p2d1f]	−1463	225	−167	−175	72
$Li\cdots H_2$	6-311G(2d,2p)	−100	−24	−8	−5	74
		−89	−24	−8	−5	
$(H_2)_2$, T-shape	[4s3p; 1s1p; 1d][a]	−346	−51	−3	−25	35
		−328	−47	−3	−25	
$(N_2)_2$, rectangular	[3s2p1d]	−3248	12244	−971	−491	73
$(PH_3)_2$	6-31G*	−1946	201	−4	−127	75
$CH_2\cdots HOH$[b]	6-31G*	−4870	1264	448	−40	75
$(HF)_2$	6-31G**	−6063	1707	−1289	*c*	75
$(H_2O)_2$	6-311++G(2d,2p)	−6276	669	−669	*c*	6

[a] 1s1p and 1d diffuse AO's are bond functions. [b] CH_2 stands for carbene. [c] With 6-31G* it was found[76] that ΔE^4 is determined completely by the ΔE^4_T term (i.e., *S*, *D*, and *Q* contributions cancel out).

values of ΔE^4. It is therefore recommended that results obtained at the MP4 level with inclusion of single, double, and quadruple excitations be carefully evaluated. There is an obvious reason for not including triple excitations: (i) the *T* term, contrary to the *D* and *Q* terms, is sensitive to the quality of basis set, (ii) the numerical evaluation of this term is time-consuming. Examples are the MP4-SDTQ and MP4-SDQ calculations on the $(H_2)_2$ dimer with the [4s3p1d] basis set: while the former calculation took 231 min, the latter required only 169 min (CPU time, VAX 780).[35] As extended complex as nitromethane dimer was studied recently[77] at the MP4-SDQ level (DZ+P basis set).

We have seen that double excitations play a dominant role in the evaluation of ΔE^{COR}. In the above-mentioned papers, all the excitations were included through the fourth order and with $(Be)_2$[69] through the eighth order. Application of the coupled cluster method[78] (CC) permits us to take the effect of doubles through the infinite order into account. The CCSD+T(CCSD) method was used[79] for evaluation of ΔE^{COR} for $(H_2O)_2$ (infinite-order effects are taken into account with the CC wave function with single and double excitations; the infinite-order effect of triple excitations is approximated by a single triple excitation evaluated with converged CCSD amplitudes). The results of the paper concerning the role of higher excitations are encouraging. In the region of the vdW minimum and at larger distances, the ΔE^{COR} has been recovered nearly completely by means of low-order perturbation theory. For O–O distances in $(H_2O)_2$ of 3.0 and 4.8 Å, the following values of ΔE^{COR}, determined with the MP4-SDTQ and CCSD+T(CCSD) methods, were found: −22.820, −22.836; −4.904, −4.862 kJ/mol, respectively.

In the light of the role of triple excitations described above, the CEPA method[80] cannot be recommended for the most accurate calculations of interaction energies. As the quadruply excited configurations are included (although only in an approximative manner), the CEPA method is size-consistent. The contributions arising from double excitations are included through the infinite order. It can be expected that the CEPA interaction energy will be close to that obtained at the third-order level of the MBPT.

Neglection of triples, on the one hand, entails problems connected with the accuracy of ΔE and, on the other hand, allows a considerable increase in the size of the vdW molecules studied. On the basis of the data listed in Table V, it is evident that there is no reason to prefer the use of the third-order level over the second-order level. For some types of intermolecular complexes mentioned in Table V, the third- and fourth-order contributions cancel out and then the use of the second-order level is justifiable. Sometimes, however, this compensation does not occur, and consequently, the third-order level is more appropriate. This compensation would appear to be present for H-bonded complexes. But before recommending use of only the second-order level, more extensive information must be accumulated.

The availability of effective computer codes for the evaluation of the second-order many-body perturbation theory (GAUSSIAN 82[61], HONDO 5/MP2[81]) has resulted in a growing number of papers employing the MP2 method for supermolecular calculations. In this respect the suitability of the HONDO 5/MP2 program should be mentioned, especially for symmetrical vdW molecules. As an example let us compare[82] the timing of HONDO 5/MP2 and GAUSSIAN 80 for the ΔE^2 evaluation for ethylene (twisted): taking the D_{2d} symmetry into account, the former program needed 7 min while the latter required 20 min (CPU time, DEC 1099 computer). For higher symmetry, this ratio is even larger; for D_{3h} symmetry can even attain 1 order of magnitude. Because the MP2 level can be attained even for medium-sized vdW molecules, it is worthwhile to analyze the method more carefully. Because the triples are not included, the coupling term between the intersystem and intrasystem correlation energies is not considered; the intersystem and the intrasystem components of ΔE^{COR} are, however, properly taken into account. Both contributions can be directly compared with the corresponding perturbation terms. The intersystem correlation energy is identical with the second-order nonexpanded Møller–Plesset dispersion energy, which consists of an attractive long-range polarization part and an exponentially decaying repulsive exchange-dispersion contribution. The intrasystem correlation energy is identical with the correlation corrections to the first-order exchange-repulsion and Coulombic energies. Of all the methods permitting us to recover some part of the correlation energy, the MP2 method is most promising for application to extended vdW molecules. It must be kept in mind that, once again, an extended basis set (at least of DZ+P quality) should be used; using smaller basis sets leads to strongly underestimated values of ΔE^{COR}.

Triple excitations play an important role in the evaluation of the correlation interaction energy. Therefore, only the methods explicitly taking these excitations into account can be recommended for accurate calculations of ΔE^{COR}. The SDTQ-CI method can be taken as a reference method; the full MP4 calculation, which is much more economic, yields comparable values of ΔE^{COR}. At a lower level of sophistication, the MP2 method, enabling us to tackle medium-sized complexes, can be recommended.

5. Approximation of the Interaction Correlation Energy by Dispersion Energy

The idea of expressing the total interaction energy as the sum of the SCF interaction energy and the dispersion energy, given by the second-order perturbation theory, is rather old.[13,83] It was hoped that the neglecting of the repulsive terms such as the intramolecular correlation corrections to the first-order exchange-repulsion and Coulombic energies is justifiable and that the respective error is smaller in absolute value than the effect of the basis set truncation on the dispersion energy. There is a growing body of evidence, however, that this is not true and may actually be a source of considerable errors.[37] It could well be asked why we analyze and test such an approach? It must be kept in mind that only this approach to the evaluation of interaction energy is routinely applicable for medium-sized vdW molecules. It was mentioned in the previous Section that the evaluation of the MP2 correlation interaction energy for symmetrical complexes is rather fast. Unfortunately, most vdW molecules possess rather low (or no) symmetry. Even the MP2 calculation is then tedious and can be carried out only for "small" medium-sized vdW molecules. Let us demonstrate this approach on vdW molecules from this class of complexes; it is assumed that the DZ+P basis set is good enough. A rather small $C_3H_6\cdots F_2$ complex has 110 MO, a larger $C_6H_6\cdots C_2H_4$ complex has 158 MO, and the H-bonded guanine···cytosine complex possesses 354 MO. There is some hope of carrying out the SCF and MP2 calculations for the first two vdW molecules, but for the last one even the SCF run is very tedious. If we need to optimize the structure of the complex (as is usually the case) we cannot at present and in the near future hope to employ the SCF+MP2 method for medium-sized vdW molecules. It must be added immediately that this is also true for the combination of SCF + E^D, if E^D is evaluated by the second-order perturbation method. This is because reasonable values of E^D can be obtained only by using the same basis set as in the case of MP2 calculation. The evaluation of E^D (i.e., the nonexpanded dispersion energy) is almost as tedious as the evaluation of ΔE^{COR} by MP2. The only efficient approach to the evaluation of the interaction energy for medium-sized complexes represents a combination of SCF method, using a minimal basis set for the evaluation of ΔE^{SCF} and an empirical method for the evaluation of E^D. The well-known expressions for the evaluation of E^D, suggested in the thirties by London,[84] Slater and Kirkwood,[85] and Müller,[86] use, e.g., ionization potentials, polarizabilities, and diamagnetic susceptibilities. The disadvantage of all these approaches is that they yield E^D values underestimated by about 50%. Further, it is inconvenient to work with subsystem characteristics, because the anisotropy of the dispersion energy is not taken into consideration. When the atomic or bond characteristics are employed, the anisotropy is partially taken into account; the dispersion energy can be obtained by using the expression:

$$E^D = -\sum_i^R \sum_j^T C_{ij} r_{ij}^{-6} \quad (5)$$

Summation over i and j is carried out over all the atoms of subsystems R and T; r_{ij} is the distance between atoms i and j and C_{ij} is a coefficient including, e.g., the polarizabilities and ionization potentials of atoms i and j. The atomic polarizabilities can be readily determined with the bond or total polarizabilities. It is, however, known that the molecular polarizability cannot be expressed simply as the sum of the atomic polarizabilities, but that the valence state of the particular atom must be considered. This idea was first developed by Miller[87] and later by Yoffe[88] and by Kang and Jhon.[89] The last cited work will be considered more closely. The authors determined coefficients C_{ij} in eq 5 using the London approximation; however, both the polarizability and the ionization potential are related to the specific valence state of the atom. Table VI lists the polarizability and ionization potential values for various valence states of atoms H, C, N, O, and P. Both characteristics originate in the experimental values. The C_6 values determined in this way agree surprisingly well with the accurate C_6 values. For the sake of illustration, the values for this coefficient will be given for the CH_4, C_3H_8, and NH_3 molecules.[89] The accurate values for the C_6 coefficient for these substances equal 7468.1, 44287, and 5133.1 (in kJ·mol^{-1}·Å^6), the use of standard London relationship (molecular characteristics) yields 6146.2, 31175, and 3357.7 while the use of the atomic characteristics yields 6889.2, 40225, and 5123.5, respectively. Coefficients C_{ij}, given in Table VI, were determined from the experimental characteristics; the coefficients can also be obtained by adjustment to already established values of the dispersion energy. In this way the coefficients for H, C, and N were evaluated.[90] The dispersion energy

TABLE VI. Values[89] of Atomic Polarizabilities (α) and Ionization Potentials (*I*) for the Following Atoms: H, C, N, O, and P

atom	valence state[a]	α (Å^3)	*I* (eV)
H	σ	0.386	13.61
C	tetetete	1.064	14.57
	trtrtrπ[b]	1.382	11.22
	trtrtrπ[c]	1.230	11.22
	trtrtrπ[d]	1.529	11.22
	didiππ	1.279	11.24
N	te²tetete	1.094	14.31
	trtrtrπ²	1.090	12.25
	tr²trtrπ	1.030	14.51
	di²diππ	0.852	14.47
O	te²te²tete	0.664	18.40
	tr²tr²trπ	0.460	17.25
	tr²trtrπ²	0.422	14.97
	te²te²te²te	1.791	6.31
P	tetetetetπ	1.743	12.09

[a] te = tetrahedral, tr = trigonal, di = diagonal. [b] Aliphatic hydrocarbons with double bond. [c] Aromatic hydrocarbon. [d] Condensed hydrocarbon.

of substituted azobenzenes was determined by the Unsöld method. In ref 91, the parameter set was extended by the values for O, F, and Cl. Here again, the Unsöld method was used to obtain the ab initio dispersion energies for the complexes formed by H_2O, CHF_3, and $CHCl_3$. The numerical values of C_{ii} (in kJ·mol^{-1}·Å^6) for H, C, N, O, F, and Cl are as follows 103.8, 2254.2, 1510.5, 882.1, 511.4, and 7033.5. The C_{ij} parameters for atoms of the various elements can be obtained as the geometric mean of the C_{ii} and C_{jj} values. Of course, there are other, in general more accurate, methods for the evaluation of the dispersion energy. The dispersion energy is obtained in the form of a multipole expansion; the individual contributions are proportional to the sixth, eighth, tenth, and higher powers of the reciprocal distance. To evaluate the first term, the dipole polarizabilities (in case of the London approximation) must be known; higher terms in the expansion are determined by means of higher polarizabilities. It is, however, hardly possible to determine higher polarizabilities experimentally. On the other hand, the polarizabilities can be calculated theoretically; the completeness of the basis set may be overcome by using the Unsöld method.[92] In this case, reasonable values of C_6, C_8, and C_{10} can be obtained by using a basis set of only DZ quality.[93] The contributions of higher terms to the dispersion energy are by no means negligible, especially in larger complexes (see, e.g., papers 94, 95). However, a serious problem arises when the multipole expansion is used for larger complexes, as the expansion of the dispersion energy starts to diverge.[94,95] This divergency can be overcome by damping the individual terms of the expansion. This is, no doubt, a sound idea, but the determination of the damping coefficients is not a simple matter. It can be carried out on the basis of knowledge of the exact dispersion energy; the C_6, C_8, C_{10}, C_{12}, ... coefficients can be easily used to establish the respective damping coefficients. Unfortunately, the exact dispersion energy is known only for the smallest complexes, H···H[96] and He···He[8,97] and correct values of the damping coefficients for these complexes exist. Under some circumstances it is possible to adopt these coefficients for evaluation of a damping procedure for similar complexes, but to use them for evaluation of a damping procedure for other types of vdW molecules is questionable.

The atom–atom expression for the dispersion energy, discussed above, yields quite accurate values of the first term in the dispersion energy expansion; higher terms are not included. Thus, these procedures yield the lower limit of the accurate dispersion energy.

Let us now analyze the error that is introduced if ΔE^{COR} is approximated by the first term in the dispersion energy expansion ($\sim R^{-6}$), which is evaluated by the atom–atom approximation. First of all, the higher terms in this expansion are neglected; this may mean neglecting a rather important portion of the attraction (20–40%), especially with larger complexes. Further, the change in the intrasystem correlation energy is not considered. This contribution consists of the correlation corrections to the first-order Coulombic and exchange-repulsion energies. Both terms may be repulsive or attractive; consequently, the change in the intrasystem correlation may also be repulsive or attractive. Mostly, however, this contribution is repulsive. Of the two terms constituting the change in the intrasystem correlation energy, the correlation correction to the Coulombic energy (E^C_{COR}) is more important at vdW minimum and at larger distances. Neglecting multipole moments higher than dipole moment and exchange effects yields the following equation[98] for E^C_{COR}:

$$E^C_{COR} = -\frac{1}{R^3}(\mu^{SCF}_{x,R}\Delta\mu^{COR}_{x,T} + \mu^{SCF}_{y,R}\Delta\mu^{COR}_{y,T} + 2\mu^{SCF}_{z,R}\Delta\mu^{COR}_{z,T}) - \frac{1}{R^3}(\mu^{SCF}_{x,T}\Delta\mu^{COR}_{x,R} + \mu^{SCF}_{y,T}\Delta\mu^{COR}_{y,R} + 2\mu^{SCF}_{z,T}\Delta\mu^{COR}_{z,R}) \quad (6)$$

where $\mu^{SCF}_{x,R}$ and $\Delta\mu^{COR}_{x,T}$ represent the xth component of the SCF dipole moment of subsystem R and the correlation correction to the xth components of the SCF dipole moment of subsystem T. When the values of the SCF dipole moment and correlation correction to the dipole moment are known, it is possible to estimate the correlation contribution to the Coulombic energy by using eq 6. A pilot estimate of the importance of this term can be carried out on the basis of values of the dipole moment evaluated at the SCF and the beyond-SCF levels. Providing the difference is small, the correlated contribution to E^C will also be small and vice versa. The beyond-SCF values of the dipole moments are usually lower than the SCF values: the HF value of the dipole moment for H_2O amounts[99] to 6.65×10^{-30} C m; the remaining difference from the experimental value (6.19×10^{-30} C m) is essentially due to the correlation energy.[99] The reduction of the dipole moment for larger molecules when passing from the SCF to the beyond-SCF level is comparable to that for water. The SCF dipole moments and the MP2 correlation corrections to them[98] (in 10^{-30} C m) for guanine, cytosine, adenine, and thymine, evaluated with the minimal basis set MINI-1, amount to 23.72, 22.94, 14.82, 8.18; −1.28, −3.17, −0.22, −0.88, respectively. Lower values of the dipole moment at the beyond-SCF level mean that the correlation correction to the Coulombic energy will be positive, i.e., repulsive.

The usefulness of the above procedure for evaluation of the interaction energy will be demonstrated on complexes formed by the DNA bases, guanine (G), cytosine (C), thymine (T), and adenine (A). A total of 28 different complexes can be formed between these bases; the largest is G···G and the smallest is C···C. Interaction energy was expressed[7] as a sum of the ΔE^{SCF} values, evaluated by using Huzinaga's MINI-1 basis set, the basis set superposition error, and the dispersion energy. The last term was evaluated by using the London formula with atomic polarizabilities and atomic ionization potentials for the respective valence state. Table VII lists values of the energy terms, evaluated at the vdW minimum.

The reliability of the data in Table VII can be questioned. As mentioned earlier, it is impossible to perform higher quality calculation for complexes of this size; it is, therefore, not possible to verify the entries in Table VII by calculating more accurate theoretical values. However, for the complexes under study, we have the rather rare possibility of comparing the theoretical data with experimental values. By field mass spectrometry, the interaction enthalpy at 300 K (ΔH_{300}) was measured[100] for the following complexes: G···C, C···C, A···T, and T···T, yielding values of −88, −67, −54,

TABLE VII. SCF Interaction Energy (ΔE^{SCF}), Basis Set Superposition Error (BSSE), Dispersion Energy (E^D), Electrostatic Energy (E^{ES}), and Interaction Energy (ΔE) for Complexes Formed by the DNA Bases Guanine (G), Cytosine (C), Thymine (T), and Adenine (A).[7] (Energies in kJ/mol)

pair[a]	ΔE^{SCF}	BSSE	E^D	BSSE + E^D	E^{ES}	ΔE
GC(WC)[b]	−97.9	16.0	−28.6	−12.6	−85.5	−110.6
GG(I)	−97.1	19.4	−28.7	−9.3	−80.5	−106.4
CC	−66.9	9.5	−32.8	−23.3	−70.9	−90.3
GG(III)	−70.7	10.3	−26.5	−16.2	−66.5	−86.9
GC(II)	−59.6	9.6	−32.1	−22.5	−58.9	−82.1
AC(I)	−56.9	9.1	−31.7	−22.6	−61.2	−79.5
GA(I)	−59.6	13.0	−30.0	−17.0	−54.6	−76.6
GG(IV)	−48.1	9.1	−33.2	−24.1	−45.1	−72.2
GT(I)	−62.6	16.0	−24.5	−8.5	−50.8	−71.1
GC(I)	−59.6	10.7	−21.4	−10.7	−60.4	−70.3
AT(RWC)[b]	−54.4	12.2	−26.8	−14.6	−48.1	−69.0
GT(II)	−61.0	16.9	−23.9	−7.0	−52.8	−68.0
AT(RH)[b]	−52.2	10.7	−26.1	−15.4	−50.3	−67.6
AT(WC)[b]	−53.9	11.0	−24.0	−13.0	−45.1	−66.9
AT(H)[b]	−52.2	10.7	−26.1	−15.4	−47.6	−66.7
AA(I)	−42.0	10.3	−34.5	−24.2	−47.8	−66.2
GG(II)	−56.7	7.0	−16.5	−9.5	−51.8	−66.2
AA(II)	−42.7	7.8	−26.8	−19.0	−44.1	−61.7
GA(II)	−39.5	8.2	−30.2	−22.0	−39.4	−61.5
GA(III)	−45.6	10.0	−25.8	−14.8	−41.5	−61.4
GA(IV)	−38.1	9.1	−31.5	−22.4	−44.3	−60.5
TC(I)	−45.6	12.8	−26.8	−14.0	−41.4	−59.6
TC(II)	−45.2	13.6	−26.0	−12.4	−41.1	−57.6
TT(III)	−46.8	15.8	−22.1	−6.3	−37.2	−53.2
TT(II)	−45.7	15.0	−21.9	−6.9	−35.6	−52.6
AC(II)	−38.2	13.7	−28.0	−14.3	−36.4	−52.4
TT(I)	−44.6	15.1	−22.5	−7.4	−35.2	−52.0
AA(III)	−21.3	10.0	−27.5	−17.5	−25.7	−38.8

[a] Cf. Figure 2. [b] WC = Watson, Crick; RWC = reversed Watson, Crick; H = Hoogsteen; RH = reversed Hoogsteen.

and −38 kJ/mol, respectively. The interaction enthalpy at 300 K and interaction energy are related as follows:

$$\Delta H_{300} = \Delta E + \Delta \mathrm{ZPE} + \Delta H_{0\rightarrow 300} \qquad (7)$$

ΔZPE and $\Delta H_{0\rightarrow 300}$ are the changes in the zero-point energy and the temperature change in ΔH when passing from 0 to 300 K. The former term is positive, i.e., decreases the value of ΔE, and the latter term is negative but its absolute value is much smaller than that of the former term. In order to evaluate ΔZPE, it is necessary to know the complete set of intramolecular frequencies as well as all the intermolecular frequencies. Experimental or theoretical evaluation of the complete set of frequencies would be very difficult. A linear relationship between ΔZPE and ΔE was found[101] for a broad set of H-bonded complexes. When adding the ΔZPE, obtained in this way, to ΔE (Table VII), the following values of theoretical interaction enthalpies for the G···C, C···C, A···T, and T···T complexes result: −94, −76, −57, and −43 kJ/mol, respectively. Evidently, the theoretical values of ΔE for the DNA base pairs given in Table VII are reasonable both in their relative order and numerically. This supports the use of the above theoretical procedure for evaluation of the interaction energy for medium-sized vdW molecules.

Let us now briefly analyze the energy characteristics listed in Table VII. The ΔE^{SCF} values for different complexes differ greatly—the ΔE^{SCF} value for the strongest complex GC (Watson–Crick) is more than 4 times larger than that for the weakest complex. The BSSE values differ less [from 19.4 kJ/mol (GG(I)) to 7.0 kJ/mol (GG(II))]. On an average, the BSSE/ΔE^{SCF} ratio for the discussed medium-sized vdW molecules is not very different from the ratio found previously[22] with the same basis set for small vdW molecules. The absolute values of dispersion energy vary less than the ΔE^{SCF} values, the ratio between the largest and the smallest E^D value being about 2. The dispersion energy is very important for all the pairs. With the strongest pairs it forms about 25% of the stabilization energy, and with weaker pairs this portion increases. With some pairs the dispersion energy amounts to more than 50% of the stabilization energy. The importance of E^D is worth mentioning because with smaller H-bonded complexes the dispersion energy constitutes not more than 20% of the stabilization energy. The dispersion energy given in Table VII corresponds to the first term in the respective expansion; the higher terms (which are attractive) are significant. On the other hand, the change in the intrasystem correlation energy is missing. It is evident from the values of SCF dipole moments

TABLE VIII. Beyond Hartree-Fock Stabilization Energies of vdW Molecules

vdW molecule	type of calculation	AO basis set	$-\Delta E$ (kJ/mol)	ref
He···He	CI		0.089	145
Ne···Ne	MP(2)	[8s4p3d]	0.136	34
Ar···Ar	MP(4)-SDTQ	[8s4p2d1f]	0.893	72
Be···Be	complete CI (only valence orbitals)	[8s5p2d1f]	7.782	49
Mg···Mg	MP(4)-SDTQ	[7s4p2d1f]	14.684	72
He···H_2	CI	He:[7s4p2d1f] H:[6s3p2d]	0.120	59
He···O_2	CEPA	He:[3s3p1d] O:[6s4p2d1f]	0.201	146
Li···H_2	MP(4)-SDTQ	6-311G(2d,2p)	0.102	74
Li···OH_2	MP(4)-SDTQ	6-311+G(2df,p)	57.61	147
Be···OH_2	MP(4)-SDTQ	6-311+G(2df,p)	23.14	147
Na···OH_2	MP(2)	6-31+G(2df,2pd)	30.8	148
Mg···OH_2	MP(2)	6-31+G(2df,2pd)	16.0	148
H_2···H_2	complete CI	[5s4p1d]	0.433	49
N_2···N_2	MP(4)-SDTQ	[3s2p1d]	1.208	73
LiH···LiH	MP(4)-SDQ	6-31G**	199	149
HF···HF	MP(4)-SDTQ	6-311++G(3df,3pd)	21.1	6
HCl···HCl	MP(4)-SDTQ	6-31+G**	6.28	76
OC···HF	MP(3)	6-311++G(2d,p)	14.02	120
N_2···H_2O	MP(3)	6-31G*	6.99	150
HF···H_2O	MP(4)-SDQ	6-31G**	42	149
HF···H_2S	MP(2)	6-31G(2d,p)	26.4	151

vdW molecule	type of calculation	AO basis set	$-\Delta E$ (kJ/mol)	ref
HCl···H_2O	MP(2)	6-31G(2d,p)	27.6	151
HCl···H_2S	MP(2)	6-31G(2d,p)	20.7	151
HF···NH_3	MP(4)-SDQ	6-31G**	54.0	149
HCl···NH_3	MP(3)	6-31G**	41.7	152
HF···PH_3	MP(2)	6-31G(2d,p)	25.2	151
HCl···PH_3	MP(2)	6-31G(2d,p)	18.2	151
HF···HCCH	MP(4)-SDQ	6-31G*	18.8	153
HCl···HCCH	MP(4)-SDQ	6-31G*	11.7	153
HF···H_2CCH_2	MP(4)-SDQ	6-31G*	19.3	153
HCl···H_2CCH_2	MP(4)-SDQ	6-31G*	12.1	153
HCl···CH_3NH_2	MP(3)	6-31G**	48.1	152
HCl···CH_3CHO	MP(2)	6-31G*	28.0	154
HCl···$(CH_3)_2NH$	MP(3)	6-31G**	52.0	152
HCl···$(CH_3)_3N$	MP(3)	6-31G**	54.9	152
H_2O···H_2O	MP(4)-SDTQ	6-311++G(3df,3pd)	22.3	6
H_2S···H_2S	MP(4)-SDTQ	6-31+G**	5.86	76
BeH_2···BeH_2	MP(4)-SDQ	6-31G**	137	149
CH_2···H_2O	MP(4)-SDTQ	6-31G*	27.4	75
H_2O···NH_3	MP(4)-SDQ	6-31G**	31.0	149
H_2O···HCCH	MP(4)-SDTQ	6-31G**	12.6	155
BH_3···BH_3	MP(4)-SDQ	6-31G**	163.7	149
NH_3···NH_3	MP(2)	6-311+G**	15.9	6
PH_3···PH_3	MP(4)-SDTQ	6-31+G**	3.35	76
NH_3···HCCH	MP(4)-SDTQ	6-31G**	15.1	155
NO_2CH_3···NO_2CH_3	MP(4)-SDQ	DZ+P	21.1	77

TABLE IX. Experimental Structural Characteristics[a]

Atom···Atom

He···He	Ne···Ne	Ar···Ar	Kr···Kr	Xe···Xe	A···B	Li···Li	Be···Be	Mg···Mg	Ca···Ca
297.5	310.2	375.9	401.2	436.2	A, B = He, Ne, Ar, Kr, Xe (A ≠ B)	267.3	245	389	428
VT[156]	DS[157]	MS, V[158]	SVC, TC[159]	DS[160]	DS[161]	AS[162]	AS[162]	AS[163]	AS[164]

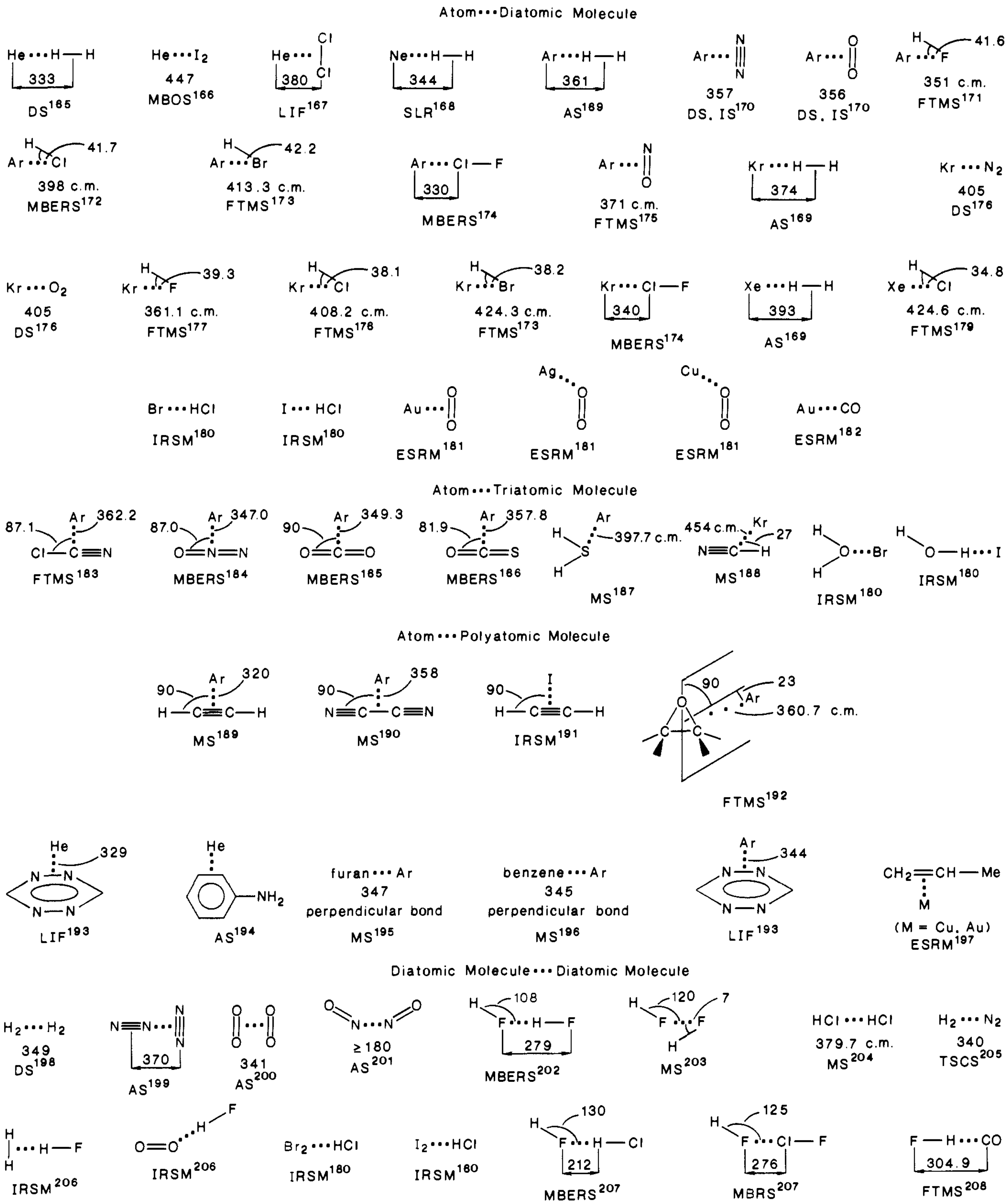
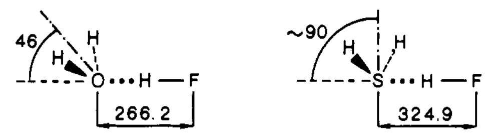


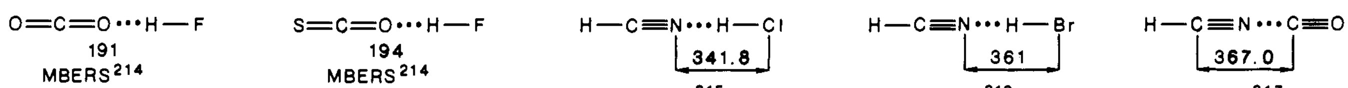
TABLE IX (Continued)

FTMS[208] | FTMS[208] | FTMS[209] | IRSM[180] | IRSM[180] | (X = Cl, Br, I) IRSM[210]

Diatomic Molecule••• Triatomic Molecule

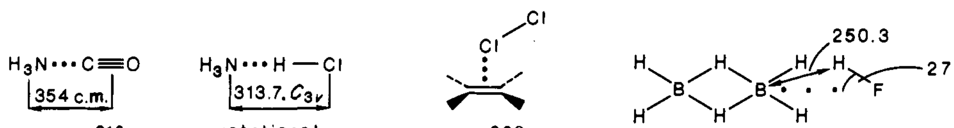


MS[211] | MS[212] | 187 MS[213]

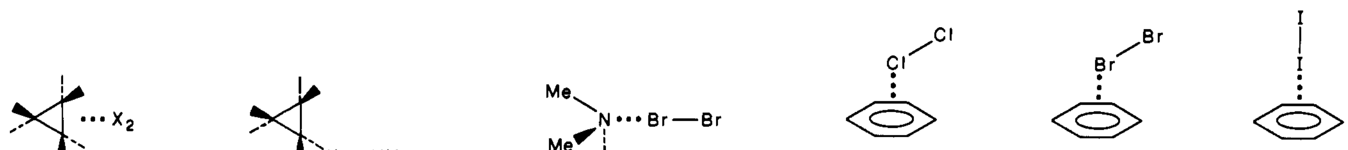


191 MBERS[214] | 194 MBERS[214] | FTMS[215] | FTMS[216] | FTMS[217]

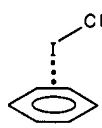
Diatomic Molecule••• Polyatomic Molecule



MBERS[218] | rotational spectra[219] | AS[220] | FTMS[221]



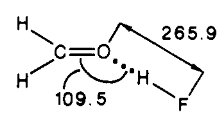
(X = F, Cl, Br) IRSM[222] | (X = Br, CN, CH_2Br, $COCH_3$, $COHCH_3$; Y = Cl, Br) IRSM[223] | ED[224] | AS[225] | AS[225] | AS[226]



AS[225]

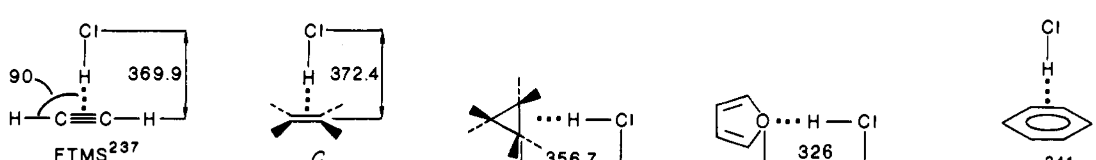
$H_3N\cdots HF$ 178, C_{3v} IRSM, MS[227]

$H_3P\cdots HF$ 330.9, C_{3v} IRSM, MS[228]



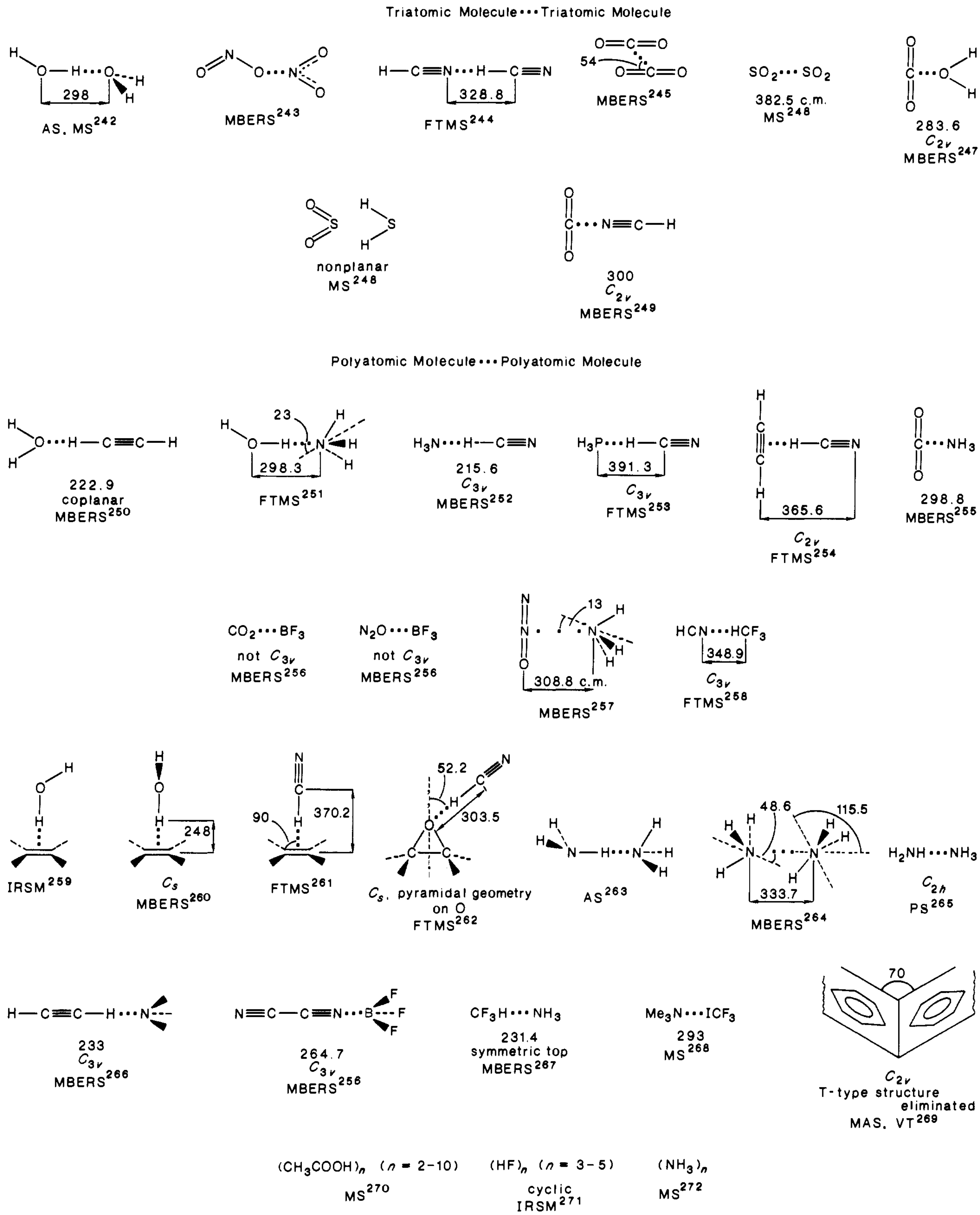
MBERS[229]

C_{2v} FTMS[230] | (X = F, Cl, Br, I) MS[231] | FTMS[232] | MS[233] | FTMS[234] | C_{2v}, coplanar FTMS[235] | MBERS[236]



FTMS[237] | C_{2v} FTMS[238] | C_{2v}, coplanar FTMS[239] | coplanar FTMS[240] | MS[241]

TABLE IX (Continued)



[a] Experimental data on the structure and geometry of vdW molecules. Bond lengths and angles are given in picometers and degrees. If not otherwise indicated, the bond length refers to the respective vdW bond; 0 c.m. designates center of mass. Abbreviations: AS = absorption spectroscopy, DS = differential scattering, ED = electron diffraction, ESRM = electron spin resonance spectroscopy in matrix, FTMS = Fourier-transform microwave spectroscopy, IRSM = infrared spectroscopy in a solid matrix, IS = integral scattering, LIF = laser-induced fluorescence, MBERS = molecular-beam electric resonance spectroscopy, MBOS = molecular-beam optical spectroscopy, MAS = mass spectrometry, MS = microwave spectroscopy, PS = photoelectron spectroscopy, SLR = spin–lattice relaxation, SVC = second virial coefficient, TC = thermal conductivity, TSCS = total scattering cross-section, V = viscosity, VT = various techniques.

TABLE X. Experimental Gas-Phase Stabilization Energies and Enthalpies

system	$-\Delta E$ (J/mol)	$-\Delta H$ (J/mol)	T (K)	ref
$(He)_2$	89.3 ± 0.8			156
$(Be)_2$	9455.8			162
$(Ne)_2$	349.2			157
$(Mg)_2$	5144.1 ± 12			163
$(Ar)_2$	1190.8			158
$(H_2)_2$	289.4 ± 14.5			273
$(HF)_2$	29300			274
$(HCl)_2$		8950 ± 0.8	230	275
$H_2O\cdots HF$[a]	30000 ± 7000	26000 ± 5000	315	276
$(CH_3)_2S\cdots I_2$[a]	30000 ± 1700	32600 ± 1700	363	277
$(C_2H_5)_2O\cdots I_2$	18000 ± 800			278
$(C_2H_5)_2S\cdots I_2$[a]	32200 ± 1600	35100 ± 1700	367	279
benzene$\cdots I_2$	7410			280
p-xylene$\cdots I_2$	10600			280
mesitylene$\cdots I_2$	13100			280
tetrahydrothiophene$\cdots I_2$[a]	35000 ± 2100	38000 ± 2100	363	281
$H_2O\cdots H_2O$[a]		15200 ± 2100	376	282
$(CH_3)_3N\cdots SO_2$	40600 ± 1700			283
$(CH_3CO)_2$[a]		13470 ± 1460	341	284
$(CH_3OH)_2$[a]		14680	375	285
furan$\cdots CO(CN)_2$[a]		10900 ± 4200	295	286
thiophene$\cdots CO(CN)_2$[a]		25000 ± 9200	295	286
$(C_2H_5)_2O\cdots CO(CN)_2$[a]		18400 ± 2100	295	286
$(C_2H_5)_2S\cdots CO(CN)_2$[a]		70300 ± 12000	295	286
tetrahydrofuran$\cdots CO(CN)_2$[a]		34000 ± 5400	295	286
tetrahydrothiophene$\cdots CO(CN)_2$[a]		59800 ± 18000	295	286
$(CH_3COOH)_2$[a]	61250			287
$(CF_3COOH)_2$[a]	57150			287
$(CF_3CH_2OH)_2$[a]		19890	338	288
tetracyanoethylene$\cdots$benzene[a]	25000 ± 1300	27600 ± 1300	298	289
tetracyanoethylene$\cdots$toluene[a]	27800 ± 300	30200 ± 300	298	289
tetracyanoethylene$\cdots$o-xylene[a]	32600 ± 100	35100 ± 100	298	289
tetracyanoethylene$\cdots$mesitylene[a]	38000 ± 2100	41400 ± 2100	363	281
tetracyanoethylene$\cdots$durene[a]	42300 ± 3300	45200 ± 3300	363	281
tetracyanoethylene$\cdots$*p*-xylene[a]	31000 ± 2100	33900 ± 2100	363	281
thymine$\cdots$thymine		38000	300	100
cytosine$\cdots$cytosine		67000	300	100
adenine$\cdots$thymine		54000	300	100
guanine$\cdots$cytosine		88000	300	100

[a] Entropy values available in the cited paper.

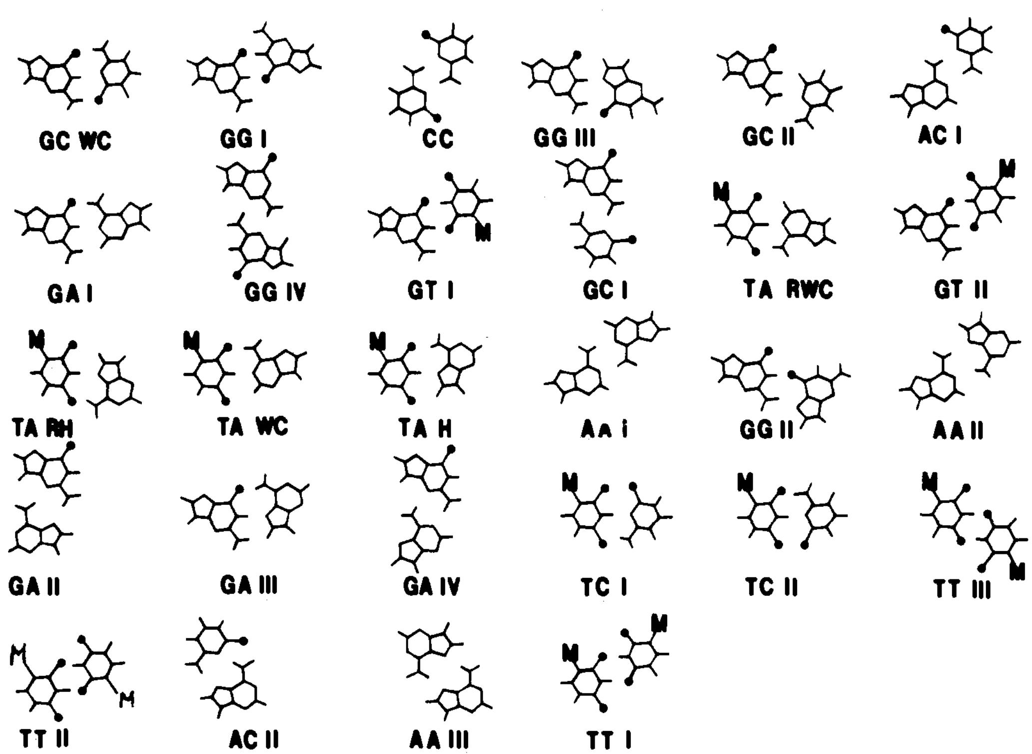


Figure 2. Structures of DNA base pairs: WC = Watson, Crick; RWC = reversed Watson, Crick; H = Hoogsteen; RH = reversed Hoogsteen.

and MP2 corrections to them, given above, that the change in the intrasystem correlation energy will be repulsive. Since the MP2 dipole moments of T and A differ[98] little from their SCF values, the dimers composed of the two bases show only a very small intrasystem correlation effect. The MP2 dipole moments of G and especially of C differ from their SCF values considerably. The correlation correction is, for dimers containing these bases, quite sizable:[98] for GC (Watson–Crick) and CC pairs it reduces the long-range interaction energy by 19 and 27%, respectively. On the basis of the surprisingly significant dispersion energy for these complexes, it seems obvious that the correlation interaction energy will be much more important in the class of vdW systems than for smaller vdW systems like $H_2O \cdots H_2O$ or $NH_3 \cdots HF$.

It has sometimes been suggested in the literature that, for H-bonded complexes, it is possible to identify the stabilization energy with ΔE^{SCF}, simply because the BSSE and E^D terms compensate. From Table VII it is evident, however, that this condition is not fulfilled; the values of (BSSE + E^D) range from −6.3 kJ/mol (TT(III)) to −24.2 kJ/mol (AA(I)). Furthermore, the addition of (BSSE + E^D) changes the order of stability of the DNA base pairs.

Expression of interaction energy as a sum of ΔE^{SCF}, evaluated with the Huzinaga minimal basis set, the respective BSSE and E^D (London formula with atomic polarizabilities and atomic ionization potentials in the respective valence state) permits study, at ab initio level, of medium-sized complexes (up to 40–50 atoms and 200–300 electrons). Despite omission of some energy contributions, the quality of the interaction energy is surprisingly good.

B. Semiempirical Methods

The previous paragraph was concluded by recommending a suitable theoretical procedure, based on ab initio SCF calculation; this procedure can be applied to complexes with up to roughly 50 atoms. Theoretical studies of larger complexes are very tempting; let us mention, e.g., the interaction between a part of DNA and a drug. Such a complex is too small for neglecting the atomic structure; obviously, the atomic structure of subsystems plays a key role in proper recognition. For complexes having several hundred atoms, the ab initio SCF method cannot be used at present or even in the near future. In chemistry, semiempirical methods of the NDO type have found wide applicability in the field of extensive systems. However, the applicability of semiempirical methods is very limited for vdW interactions. These methods were parametrized for covalent interactions and are too rough for calculation of vdW interactions. Geometry optimization of the water dimer using the CNDO or INDO method yields a peroxide-type structure, $H_2O \cdots OH_2$, as energetically most favorable. Obviously, structural and energy characteristics of this sort are meaningless. The ab initio SCF method yields the correct structure for the water dimer. Larger complexes, where it is impossible to verify the result by ab initio method, represent a greater problem. In general, it is never clear whether the result is an artefact of the method or whether it reflects the real structure. Semiempirical methods cannot be used if it is first necessary to determine the structure of the vdW molecule; they can be considered for calculation of some properties (e.g., vibrational frequencies) of a given conformation of a vdW molecule. There are several reasons for the failure of semiempirical methods.[102,103] The most serious is the complete neglect of the overlap between the orbitals of two atoms, which leads to strong underestimation of the repulsion (the exchange-repulsion term is not included).

C. Empirical Methods

The Lennard-Jones (6–12) potential[104] (eq 8) is the most frequently used empirical potential:

$$\Delta E = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (8)$$

where σ and ϵ are constants with the dimensions of length and energy, respectively; σ is the distance at which $\Delta E = 0$, and ϵ is the depth of the potential minimum. Parameters ϵ and σ are determined with suitable experimental quantities most often the second virial coefficient and the viscosity coefficient, and more recently by elastic scattering of molecular beams. The potential in the form of eq 8 is valid for the interaction of two atoms or two spherical nonpolar systems (e.g., CH_4). In this case, the total interaction energy results solely from the attractive dispersion energy and repulsive exchange-repulsion energy. We have seen that the first term in the expansion of the dispersion energy is proportional to the sixth power of the reciprocal distance. The exchange-repulsion term is proportional to the intersystem overlap, which is known to decrease very rapidly with increasing distance. This decrease can be approximated either by a higher power of the reciprocal distance or by an exponential dependence on the distance. Hence, both the terms in eq 8 correctly describe the total interaction energy of the two atoms or two spherical nonpolar systems; the use of the empirical potential in form of eq 8 is therefore justifiable. The same is true of another, widely used potential, the Buckingham potential:[104]

$$\Delta E = b\,\exp(-ar) - cr^{-6} - c'r^{-8} \qquad (9)$$

where a, b, c, and c' are constants.

Passing from the above-mentioned simple complexes to more complicated ones (consisting of, e.g., two polar subsystems) involves serious complications. First of all, the interaction energy is no longer fully described by the sum of the dispersion and exchange-repulsion energies; the Coulombic and induction energies are also important. Further, it is not possible to disregard the atomic structure of the subsystem. A solution would be to consider the subsystem atomic structure and to express the total interaction energy as a sum of the dispersion, repulsion, Coulombic, and induction energies. The question remains, however, whether and in which terms to use empirical parameters. Should these parameters be used only in the dispersion and repulsion terms (as in the Lennard-Jones potential) and perturbation expressions be used for Coulombic and induction terms? This seems at the first glance to be physically correct; the opposite is true, however. It must be kept in mind that empirical parameters for the dispersion and repulsion terms were fitted simultaneously on the basis of the interaction of nonpolar systems. Addition of other energy terms inevitably disturbs the balance between parameters describing the dispersion and repulsion terms. Such a treatment would be inconsistent: physically correct Coulombic and induction energies are added to the physically incorrect dispersion and repulsion terms (only the sum of those terms may be correct with nonpolar systems). It is therefore not correct to take the dispersion or repulsion term separately from either the Lennard-Jones or Buckingham potentials. The only way to overcome this problem is to adjust the parameters for all the energy terms simultaneously. Frequently, the interaction energy is obtained as a sum of the dispersion, repulsion, and Coulombic energies; these terms are proportional to r^{-6}, r^{-12}, and r^{-1}.

The parameters of this potential, as well as parameters of the Lennard-Jones or Buckingham potentials can be obtained experimentally (see above). We need to know, however, a sufficient amount of experimental data in order to adjust three or four parameters, with the Lennard-Jones and Buckingham potentials, or more, with a more general potential. This, however, represents a serious problem. Experimental data is sufficient for parametrization of a single-purpose potential, e.g., a potential describing the interactions among one sort of molecules, most frequently water. It would not be expedient to go into detail here, and only the widely used potentials for water given by Ben-Naim and Stillinger,[105] Shipman and Scheraga,[106] and Malenkov[107] will be mentioned. Sufficient experimental data is not available, however, for parametrization of multipurpose potentials. This difficulty can be overcome because quantum chemical calculations of the interaction energy between different subsystems can yield a sufficiently large set of data for parameter adjustment. For years, Clementi has been a pioneer in this new type of parametrization of empirical potentials. As this is a very promising method of empirical potential parametrization, the basic approach will be outlined.

Clementi and coauthors studied[108] the hydration of biomolecules. An empirical potential in the form of eq 10 was assumed:

$$\Delta E = \sum_i \sum_j (-A_{ij}^{ab} r_{ij}^{-6} + B_{ij}^{ab} r_{ij}^{-12} + C_{ij}^{ab} q_i q_j r_{ij}^{-1}) \quad (10)$$

The first summation extends over all the atoms in the biomolecule and the second one over the water atoms; A, B, and C are parameters that are adjusted by using the theoretically determined values for ΔE, r_{ij} is the distance between atom i of biomolecule and atom j of water, and, finally, q_i and q_j are the charges on atoms i and j. Superscripts a and b distinguish not only the atom specificity but also various valence states of a given atom. Interaction energy ΔE and charge q were found by using the ab initio SCF calculation with a minimal basis set. Formally, the individual terms in eq 10 correspond to the dispersion, repulsion, and electrostatic terms. However, as all the parameters were adjusted simultaneously, there is no sense in considering the physical meaning of the individual terms. Since a large number of different types of the given kind of atom (called classes) must be distinguished in the biomolecule, and since parameters A, B, and C must be known for all of them, a large number of calculations for the SCF interaction energy must be carried out. The water molecules may be located in a very large number of very different positions and orientations with respect to the rigid biomolecule. For example, for the interaction of all 22 amino acids occurring in proteins with water molecule, 1960 calculations of the SCF interaction energy were carried[109] out.

Clementi and co-workers introduced a very promising new method for parametrization of the empirical potential and applied it to the process of hydration of biomolecules. This method can yield not only the parameters for the biomolecule–water interaction but also urgently needed parameters for biomolecule–biomolecule interactions. The main advantage of this procedure is that an arbitrary amount of data can be generated for parameter adjustment. Some criticism may be made of the interaction energies used by Clementi et al. The authors used the SCF interaction energy that was not corrected for the basis set superposition error. Further, the interaction correlation energy or the dispersion energy was not included. These two corrections are not computationally difficult and lead to better quality estimates of the total interaction energy. Another problem is connected with the charges used by Clementi et al.[109] in the term for the Coulombic energy (eq 10). The charges were obtained from ab initio SCF calculations using a minimal basis set by Mulliken population analysis. It is well known that these charges are too small and rather uniform; consequently, their products divided by the respective distances yield underestimated values of the electrostatic energy. Very promising values of the atomic charges were obtained from the molecular electrostatic potential (see the next paragraph); these charges are not only larger but they are significantly less uniform in comparison with those derived from Mulliken population analysis. Finally, the transferability of empirical parameters should be investigated. The idea of Clementi and co-workers was to first derive the pair potential from the interaction of the biomolecule with water. In the second step, the pair potential will be applied to hydration of another biomolecule, providing that the atom in the "new" biomolecule will have the same environment as the "old" one. Despite the division of atoms into numerous different classes (specifically, the H, C, N, and O atoms of amino acids were divided[109] into 23 different classes), the transferability of the parameters may not be justified. Let us mention, as an example, the study[7] of the DNA base pairs. It was found[7] that, e.g., the guanine···guanine and thymine···thymine dimers, containing the same type of the C=O···H—N H-bonds, differ greatly in their stability (−122 and −67 kJ/mol, respectively). The net charges on the atoms forming the H-bonds are very similar for guanine and thymine, and further, the "environment" of these atoms is the same in both the dimers. Similarly, the adenine···adenine, guanine···guanine, and cytosine···cytosine complexes, containing the same type of the N–H···N H-bonds, differ greatly, their stabilization energy being −36.4, −48.1, and −66.9 kJ/mol, respectively. Again, the charges and environment of the atoms forming the H-bond are similar. On the basis of transferability, using the above-mentioned type of empirical potential (eq 10), we would expect to obtain very similar stabilization values for dimers with the same H-bonds.

Empirical potentials have a broad applicability especially in computer experiments of the Monte Carlo and molecular dynamics types. Reasonable parameters can be found on the basis of both experimental and theoretical characteristics. The potential based on the experimental data has an advantage in that the pair potential effectively includes the many-body terms. Usually, there is insufficient experimental data for adjusting the parameters of multipurpose potential. If theoretical characteristics are used for adjusting the empirical parameters, attention should be paid to the quality of the theoretical interaction energy: SCF and correlation interaction energies should be included and both the values should be corrected for the respective basis set superposition error. Further, carefully selected charges should be used in the electrostatic part of the empirical potential. Here, the use of charges derived from molecular electrostatic potential is recommended. Finally, careful attention must be paid to the transferability of the empirical parameters. Generally, significantly higher accuracy is expected with single-purpose potentials.

D. Electrostatic Approximation

In the electrostatic approximation, SCF interaction energy is approximated by the electrostatic term alone. Clearly, the approximation can be used for complexes where the electrostatic (Coulombic) energy is dominant; it cannot be used for the interaction of nonpolar systems. Even if the electrostatic term is dominant, the remaining terms (induction, exchange-repulsion) are by no means negligible. Here, again, the compensation effect plays a role. The electrostatic approximation has long been known, but it has never been carefully tested except for hydrogen-bonded complexes.[110] The results of this study were surprising; it was found that the electrostatic term agreed very well with the nonempirical ΔE^{SCF} value in the entire range from large distances up to the vicinity of the vdW minimum. At these distances, the angular dependence of the electrostatic term is also in reasonable agreement with the corresponding dependence of ΔE^{SCF}. Clearly, at distances smaller than that corresponding to the region of the vdW minimum, the electrostatic approximation must not be used. These findings explain the success of the electrostatic approximation when used properly and also its complete failure when used in regions where it is not applicable. It must be realized that the electrostatic approximation and the molecular electrostatic potential cannot even qualitatively predict the position of the vdW minimum. If, however, the position of the vdW minimum is known, the electrostatic approximation can then yield useful data on the stabilization energy. The applicability of the approximation was recently carefully investigated by Buckingham and coworkers.[111,112] The electrostatic energy of various vdW molecules was determined in terms of point charges, point dipoles, and point quadrupoles, obtained from the SCF charge densities of the subsystem. The electrostatic energy agrees well with the SCF interaction energy up to the region of the vdW minimum but, as expected, does not yield the position of vdW minimum, as already mentioned. The authors solved this problem very simply: the intermolecular distance at the vdW minimum was calculated as the sum of the vdW atomic radii recommended by Pauling. The relative orientation of the molecules was determined by using the electrostatic approximation. Good agreement with experiment was attained for all the studied complexes. These results support the applicability of the electrostatic approximation; the electrostatic energy should, however, be evaluated accurately. In the papers mentioned above,[111,112] it was necessary to include point charges, point dipoles, and point quadrupoles. The evaluation of higher point multipoles is not an easy task; further, if more than the first term of the expansion of electrostatic energy is employed, the numerical calculations for larger subsystems are tedious. It would therefore be desirable to calculate the electrostatic term from monopoles (charges) alone. We have seen above that charges derived from the Mulliken population are not suitable; the charges obtained on the basis of the molecular electrostatic potential or the natural population analysis seem to be very promising. In the former approach,[113-115] the molecular electrostatic potential for a subsystem is first evaluated from the ab initio SCF wave function. In the second step, arbitrary point charges are placed either at all the atoms or at other sites (e.g., at lone pairs) and an optimization procedure is used to fit the electrostatic potential calculated from these charges to that determined from the SCF wave function. The point charges, determined in this way, effectively include the higher point multipoles. In ref 116 and 117 the point charges located at the atoms were determined by the above-mentioned procedure for the following molecules: H_2O, CH_3OH, $(CH_3)_2O$, H_2CO, NH_3, $(CH_3O)_2PO_2^-$, deoxyribose, ribose, adenine, 9-methyladenine, thymine, 1-methylthymine, guanine, 9-methylguanine, cytosine, 1-methylcytosine, uracil, 1-methyluracil and ethane, propane, *n*-butane, dimethyl ether, methyl ethyl ether, tetrahydrofuran, imidazole, indole, deoxyadenosine, base paired dinucleoside phosphates, insulin, and myoglobin. Comparing the charges derived from the molecular electrostatic potential with those evaluated by means of Mulliken population analysis, we find that the first ones are considerably larger, sometimes even by a factor of 2.5. The natural population analysis[118] is an alternative to Mulliken population analysis but it describes better the electron distribution in a molecule; further, it exhibits improved numerical stability. The natural population analysis was employed in studies of different vdW molecules: $(H_2O)_2$,[119] CO···HF,[120] and binary complexes of HF, H_2O, NH_3, N_2, O_2, F_2, CO, and CO_2 with HF, H_2O, and NH_3.[121] The numerical stability of atomic charges derived from the natural analysis were studied[122] for H_2O, H_2CO, and CH_3OH molecules. It was shown that minimal basis sets underestimate the charge distribution; however, already the split-valence basis sets give reasonable values of atomic charges comparable to those obtained with extended basis sets. It was further shown[122] that the 3-21G atomic charges of adenine, guanine, thymine, cytosine, and $(CH_3O)_2PO_2^-$, obtained by natural population analysis, agreed fairly well with the atomic charges derived from the molecular electrostatic potential.

The applicability of charges derived from the molecular electrostatic potential was carefully examined[7] for pairing of the DNA bases. From Table VII it can be seen that the E^{ES} values agree reasonably with the ΔE^{SCF} values. As mentioned above, it is impossible to optimize the complex geometry with the electrostatic approximation; therefore the E^{ES} term must be evaluated at the minimum determined by the SCF interaction energy. For all the 28 DNA base pairs presented in Table VII, the electrostatic energy leads to better agreement with the SCF interaction energy than several empirical potentials. A fair estimate of the total interaction energy for any pair of DNA bases can be obtained as the sum of E^{ES}, evaluated with point charges derived from the molecular electrostatic potential, and the dispersion energy (London formula utilizing the atomic polarizabilities and atomic ionization potentials for the respective valence states). The geometry of a "new" pair can be estimated on the basis of the fact[7] that the length of a certain type of hydrogen bond (e.g., N–H···N) differs only slightly for different complexes. This is in agreement with the idea to use the vdW atomic radii for estimation of the geometry of vdW minima. The electrostatic energy corresponding to interaction between two subsystems can be expressed in terms of the monopoles and multipoles of the two subsystems. It can also be expressed as follows:

$$E^{ES} = \int V_A(\mathbf{r}_2)\gamma_B(\mathbf{r}_2,\mathbf{R}_\beta)\,d\mathbf{r}_2 \quad (11)$$

where

$$V_A(\mathbf{r}_2) = \int \frac{\gamma_A(\mathbf{r}_1,\mathbf{R}_\alpha)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,d\mathbf{r}_1 \quad (12)$$

γ_A is an element of the density matrix, $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ are vectors determining the positions of nuclei α and β with charge Z_α and Z_β (in subsystems A and B). $V_A(\mathbf{r}_2)$ is known as the molecular electrostatic potential of molecule A. This quantity describes the interaction of a proton with the molecule A. When points with the same potential are connected, isopotential curves are obtained. The molecular electrostatic potential[123] and molecular electrostatic field[124] (describing the interaction of a dipole with the molecule) are effectively connected with property of only one subsystem. The electrostatic approximation, reflecting the properties of both subsystems, is, therefore, clearly superior.

The approximation of the SCF interaction energy by the electrostatic term, if properly used, yields surprisingly good results. The electrostatic energy should be calculated correctly, i.e., the higher terms of the expansion should also be included. Problems connected with the evaluation of higher multipole moments can be overcome by using point charges derived from the molecular electrostatic potential. Reasonable values of the total interaction energy are obtained by adding the dispersion energy to the electrostatic energy.

The electrostatic approximation does not allow for geometry optimization; the geometry of the vdW minimum can be estimated from the vdW atomic radii. The other way of estimating the geometry of the vdW minimum is based on the assumption that the lengths of some types of H-bond do not differ much in different complexes (containing this type of H-bond).

E. The Localization and the Nature of Stationary Points

Investigation of portions of potential energy surfaces (PES) and search for stationary points have belonged for about 15 years to routine problems of computational quantum chemistry. In principle, it makes no difference if common or vdW molecules are treated. Analytical higher derivatives of potential energy with respect to Cartesian coordinates are commonly used in potential energy geometry optimization, in characterization of the nature of stationary points, and for including a part of anharmonicity in treatment of the vibrational problem. Procedures described in the literature concern closed and open shell systems at the Hartree–Fock and beyond Hartree–Fock levels.[125–132]

A few specific remarks on vdW species are expedient.[133] Frequently several local minima occur on PES even with simple vdW systems; their number increases rapidly with increasing complexity of the systems under study. Moreover, the minima are mostly shallow, i.e., anharmonic and separated by relatively low-lying saddle points. This circumstance makes the localization of stationary points on vdW surfaces rather tedious. When various computer programs are used for molecular geometry optimization, it is necessary to use them with special caution because otherwise quite a few minima can escape. There are some more difficulties. In general, the role of electron correlation is significant and with true vdW molecules the correlation energy represents the only binding component of the total interaction energy. Therefore the procedure mostly used for common molecules, i.e., localization of the stationary point of HF surfaces and improving their energy by adding correlation energy, cannot be used. On the other hand, direct search for stationary points on a correlated PES is tedious and expensive but with small, true vdW species represents the method of choice. With vdW molecules it is sometimes impossible to use the gradient optimization and the point-by-point method should be applied. There are two reasons for it: first, because of the necessity to optimize the corrected ΔE values (i.e., the values including BSSE at each point) and, second, because of the flatness of the potential energy surface.

Further, two instructive examples will be mentioned. The first demonstrates that "chemical intuition" or "chemical feeling" are of little assistance in localization of stationary points on the vdW energy hypersurface. The interaction of two hydrogen molecules has long attracted the attention of theoreticians and the first nonempirical calculations were carried out in the early seventies.[134,135] The authors have investigated four structures of the dimer: linear, tetrahedral, rectangular, and T-shaped; the last structure was shown to be the most stable, partially because of stabilization by two quadrupoles. Since then, several papers[136–143] have been devoted to the dimer and more and more sophisticated methods for evaluation of interaction energy have been employed. In the majority of the papers, the four above-mentioned structures of the dimer were studied. There is, however, no a priori reason to prefer these highly symmetrical structures over other, less symmetrical ones. Clearly, the $(H_2)_2$ energy hypersurface must be studied systematically and, further, the nature of the stationary points should be determined. Provided that the geometry of the H_2 molecule is kept fixed, there are four internal degrees of freedom within the $(H_2)_2$ dimer (cf. Figure 3). Fifteen structures were chosen[71] on the energy hypersurface; these structures are depicted in Figure 4. The T-shaped and rhomboid structures are the most favored; the other three structures from the original set are higher in energy. For the T-shaped and

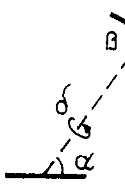


Figure 3. Internal degrees of freedom of the $(H_2)_2$ dimer.

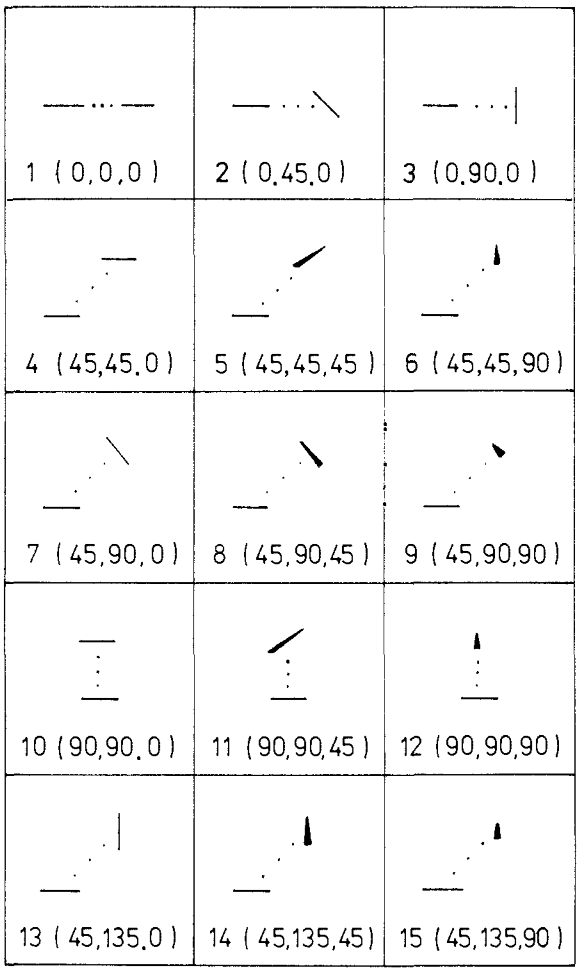


Figure 4. Structures of the $(H_2)_2$ dimer. The α, β, and δ angles (cf. Figure 3) are specified in parentheses.

rhomboid structures, the force constant matrices were constructed and the FG problem solved.[71] With the first structure all the eigenvalues are positive; the rhomboid structure has one negative eigenvalue. This result permits us to conclude that the T-shaped structure is the energy minimum while the rhomboid structure corresponds to a saddle point (separating two equivalent T-shaped structures). The other structures correspond neither to the energy minima nor to saddle points; they correspond to the local maxima or saddle points of higher order.

The second example concerns the quality of the energy calculation used for determination of the nature of the stationary points. Electron correlation has[144] a considerable influence, not only on the relative stability of lithium isocyanide (1), lithium cyanide (2), and the bridged form (3) (Figure 5) but also on the nature of the stationary points. While, according to Hartree–Fock theory, structure (1) is the most stable minimum, (2) is another minimum, and (3) is a saddle point; MP4-SDTQ optimization indicates (3) to be the deepest minimum, (1) another minimum and (2) a saddle point.

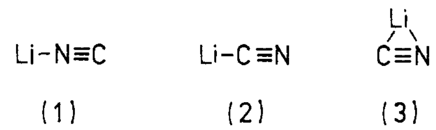


Figure 5. Structures of lithium isocyanide (1), lithium cyanide (2), and the bridged form (3).

The triatomic molecule comprising a lithium atom bound to a CN group is rather similar to a vdW molecule: very little energy is needed to move the lithium cation around the CN^- system.

V. Prospects

It seems possible that the performance of supercomputers of the eighties might correspond to the performance of small computers at the end of this century. In spite of this possibility it would be probably wrong to believe that theoretical procedures, which work for small vdW systems, might be used in a straightforward way for large complexes. The complexes consist mostly of numerous atoms because of either size of the subsystems or a large number of the small subsystems. There are two possibilities how to treat these intermolecular complexes which are topical for chemistry and molecular biology. Neither of the two possibilities is based on dirrect solution of the Schrödinger equation. The first one requires introduction of a sophisticated potential, the parameters of which can be obtained quantum chemically. In connection with, e.g., solvation phenomena, the entropy term must not be introduced a posteriori but potential of mean force must be used from the very beginning. The second possibility involves introduction of methods of another type, e.g., methods of the physics of a continuum.

No doubt, improvements of currently used quantum chemical methods are to be expected. First of all new, more efficient algorithms for the solution of the SCF problem are necessary. Second, significant development is highly desirable with beyond-SCF methods, where new, more accurate and efficient procedures are developed.

Real progress in analyzing some fundamental processes in chemistry (e.g., solvation and surface phenomena, catalysis) and in molecular biology is conditioned by deeper understanding of vdW interactions. Therefore, it is desirable to pay significantly more and deeper attention to education of the young generation in the field of van der Waals interactions.

VI. Summary

A. The summary of computational results is given in Table VIII.

B. The summary of experimental structural characteristics is given in Table IX.

C. The summary of experimental gas-phase stabilization energies and enthalpies is given in Table X.

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